ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

STYRENE - BUTADIENE RUBBER / HALLOYSITE NANOTUBES NANOCOMPOSITES MODIFIED BY ITACONIC ACID

M.Sc. THESIS

Gizem UZAN

Department of Polymer Science and Technology

Polymer Science and Technology Programme

Thesis Advisor: Prof. Dr. Nurseli UYANIK
Co-Advisor: Asst. Prof. Dr. Bağdagül KARAAĞAÇ

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

İTAKONİK ASİTLE MODİFİYE EDİLMİŞ STİREN - BÜTADİEN KAUÇUK / HALOYSİT NANOTÜP NANOKOMPOZİTLERİ

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To my family,

FOREWORD

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Chemical Engineer

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ABBREVIATIONS

SBR	**:** Styrene-Butadiene Rubber
CB	**:** Carbon Black
HNTs	**:** Halloysite Nanotubes
IA	**:** Itaconic Acid
DSC	**:** Differential Scanning Calorimeter
NR	**:** Natural Rubber
T_g	**:** Glass Trasition Temperature
MDR	**:** Moving Die Rhometer
MH	**:** Maximum Torque Value
SEM	**:** Scanning Electron Microscope
NR	**:** Natural Rubber
BR	**:** Polybutadiene
IR	**:** Polyisoprene
IIR	**:** Butyl Rubber
BIIR	**:** Brominated Butyl Rubber
CIIR	**:** Chlorinated Butyl Rubber
UV	**:** Ultra Violet
EPDM	**:** Ethylene-Propylene-Diene Rubber
NBR	**:** Acrylonitrile-Butadiene Rubber
CR	**:** Polychloroprene Rubber
FKM	**:** Floroelastomer Rubber
MQ	**:** Methyl Silicone
VMQ	**:** Vinyl Methyl Silicone
PMQ	**:** Phenyl Modified Silicone
E-SBR	**:** Emulsion Styrene-Butadiene Rubber
S-SBR	**:** Solution Styrene-Butadiene Rubber
PHR	**:** Per Hundred Rubber
TMTD	**:** Tetramethlythiuram Disulfide
ASTM	**:** American Society for Testing and Materials
MWCNTs	**:** Multi Walled Carbon Nanotubes
MAA	**:** Methacrylic Acid
SA	**:** Sorbic Acid
TEM	**:** Tranmission Electron Microscope
RH	**:** Complex of Resorcinol and Hexamethylenetetramine
M-HNTs	**:** Modified Halloysite Nanotubes
FTIR	**:** Fourier Transform Infrared Spectroscopy
MPS	**:** γ-Methacryloxypropyltrimethoxysilane
IPPD	**:** N-İsopropyl-N'-Phenyl-p-Phenylene-Diamine
TMQ	**:** 2, 2, 4-Trimethyl-1, 2-Dihydroquinoline
ZnO	**:** Zinc Oxide
ML	**:** Minimum Torque
ts_2	**:** Scorch Time

t_{90}	**:** Time to Reach 90% of Maximum Torque
CLD	**:** Crosslinking Density
E	**:** Young Modulus
CRI	**:** Cure Rate Index
MPa	**:** Mega Pascal
LOI	**:** Limiting Oxygen Index

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STYRENE - BUTADINE RUBBER / HALLOYSITE NANOTUBES NANOCOMPOSITES MODIFIED BY ITACONIC ACID

SUMMARY

Rubbers are very important class of polymeric materials. It is commonly used for its low weight, elasticity and processabilty. Styrene-butadiene rubber (SBR) is a type of synthetic rubber and it represents half of all synthetic rubber production. SBR is not sufficient in common applications without compounding with reinforcing filler. Favourite fillers used in SBR compounds are carbon black (CB), silica and clays. Rubber-clay nanocomposites have been widely investigated by various researchers. The nanocomposites with nanosized clay particles provide high mechanical properties, enhanced thermal stability, improved gas barrier properties, high flame retardency, decreased solvent uptake as well as increased chemical and shape memory properties. Halloysite nanotubes (HNTs) are among nano clays with large L/D ratio which provide improved properties for polymers. Due to low compatibility with rubber macromolecules, HNTs decrease dispersion quality and show poor interfacial interaction in rubber matrices without surface modification. There have been some attempts for improving the performance of SBR/HNTs nanocomposites with reactive modifiers e.g. sorbic acid (SA) and methacrylic acid (MAA). Beside this, limited studies, which HNTs and CB were used together in rubber compounds, can be found in literature.

In this study, SBR – HNTs compounds were prepared without and with CB. Effects of itaconic acid (IA) have been evaluated as a modifier between HNTs and SBR matrices in SBR/HNTs and SBR/HNTs/CB nanocomposites. Total number of compounds were 15 (9 of them without CB, remaining with CB). HNTs amount was between 0-30 phr and IA amount was between 0-5 phr for compounds which are without CB. HNTs amount was 0-20 phr, IA amount was 0-1 phr and CB amount was 20-40 phr for compounds which are with CB. Compounds were prepared by using laboratory type two roll mill. Differential scanning calorimeter (DSC) was used to determine the glass transition (T_g) and curing peak temperatures (T_p) of the compounds. Curing peak temperatures increased by adding IA. The curing time and curing characteristics of compounds were obtained by using moving die rheometer (MDR). Curing times were different for compounds depending on their HNTs, IA or CB contents and they were between 2.5-10 minutes. Maximum torque value (MH) was affected by HNTs, IA and CB amounts but minimum viscosity did not change significantly. Density measurements were done to determine the mass of compounds which will be moulded at hydraulic hot press. The compounds were cured at hydraulic hot press at 180 ^{o}C for own pre-determined curing times. Mechanical properties of nanocomposites (tensile strength, elongation at break, Young's modulus) were obtained with a tensile test machine and crosslinking densities were procured with Young's modulus values. Depending on content of nanocomposites,

mechanical properties exhibited discrepancies. Hardness values were measured by using a Shore A type durometer. Morphological properties of the nanocomposites were obtained with a scanning electron microscope (SEM). It can be said that with SEM images, better dispersion behaviour for HNTs can be attained with existence of IA. The flammability properties of nanocomposites were measured with limiting oxygen index (LOI) equipment. Nanocomposites had better flammability properties by HNTs adding.

İTAKONİK ASİTLE MODİFİYE EDİLMİŞ STİREN-BÜTADİEN KAUÇUK (SBR) / HALOYSİT NANOTÜP (HNTs) NANOKOMPOZİTLERİ

ÖZET

Kauçuklar, polimerik malzemeler içinde önemli bir sınıftır. Çapraz bağlanabilen, yüksek molekül ağırlıklı moleküllerden oluşurlar. Çapraz bağlanma, kauçuğun kimyasal yapı değişikliğine uğrayarak (vulkanizasyon reaksiyonu) ve geri dönüşümsüz olarak elastik özelliklere sahip bir duruma gelmesi ve getirilmesi işidir. Vulkanizasyon öncesi yüksek plastik özellikler, vulkanizasyon sonrası yerini yüksek elastik özelliklere bırakır. Kauçuğun çapraz bağlanmış halinin çapraz bağ miktarı çok yüksek değilse, orijinal şeklini muhafaza edebilir ve üzerine uygulanan kuvvet kaldırıldığında eski şeklini kazanabilir yani elastiktir. Vulkanize kauçuğun özellikleri çapraz bağlanma şekline ve yoğunluğuna bağlıdır. Bu özelliğinin yanı sıra hafif olmaları ve kolay işlenebilirlikleri yaygın olarak kullanılmalarının sebeplerindendir Ayrıca, kauçuktan üretilmiş ürünlerin yerine kullanmak için başka bir kauçuk malzeme dışında malzemelerin alternatif olarak kullanılması güçtür. Kauçklar, doğal ve sentetik kauçuklar olmak üzere iki gruba ayrılırlar. Poliisopren kauçuk (IR), butadiene kauçuk (BR), akrilonitril-bütadien kauçuk (NBR), etilen-propilen-dien kauçuk (EPDM), polikloropren (CR), butil kauçuk (IIR) ve stiren-bütadien kauçuk (SBR), başlıca kullanılan sentetik kauçuklardandır. Bunarın dışında özel amaçlar için kullanılan florosilikon kauçuk, akrilik kauçuk, etilen-akrilik kauçuk, polinorbornen, hidrojenize nitril kauçuk, karboksilli nitril kauçuk, florokarbon kauçuk gibi çeşitleri de vardır. SBR, stiren ve butadien monomerlerinin emülsiyon ya da süspansiyon polimerizasyonuyla elde edilen sentetik bir kauçuk türüdür. Bütadien/stiren oranı genellikle 75/25'tir. SBR, genelde 250000-800000 arasında ortalama molekül ağırlığı değerlerine sahip olarak üretilir. Polimerizasyon tipi, SBR'nin özellikleri üzerinde etkilidir. Örneğin; çözelti polimerizasyonunda elde edilen SBR'nin molekül ağırlığı dağılımı dar iken, emülsiyon polimerizasyonuyla elde edilen SBR'nin molekül ağırlığı dağılımı geniş olmaktadır. SBR'nin yapısındaki stiren oranı da özelliklerini etkileyen bir başka parametredir. SBR'nin yapısındaki stiren miktarı arttıkça elastikiyeti azalır, işlenmesi daha zor hale gelir fakat mekanik özellikleri, içinde daha az stiren bulunan SBR'ye gore daha iyidir. Yapı, içerisinde stiren halkası bulundurduğu için düzensiz olduğundan kristallenmeye yatkın değildir. Birçok uygulamada doğal kauçuk (NR) yerine kullanılır. SBR, NR'a göre daha kolay işlenebilir. Elastik davranışları NR kadar iyi olmasa da aşınma ve ısıya dayanım özellikleri NR'tan daha üstündür. Polar olmayan sıvılara, çözücülere, seyreltik asit ve bazlara dayanıklı olup yakıt ve yağlara dayanıksızdır. Tüm sentetik kauçuk üretiminin yarısına karşılık gelir ve sanayide en çok otomobil lastiği üretiminde kullanılır. İstenilen özelliklere göre ayarlanmış, kauçuk ve diğer hammaddeler ile katkı maddelerinden oluşan, vulkanize edilebilen bir karışımdır. Kauçukların tek başına kullanılması mümkün değildir ve bazı katkı maddeleriyle karışım haline getirilmesi gerekir. Bu katkı maddeleri, çapraz bağlanma maddeleri (çapraz

bağlanma ajanları, aktivatörler, hızlandırıcılar, geciktiriciler), güçlendirici ya da güçlendirici olmayan dolgular, plastikleştiriciler, proses kolaylaştırıcılar, yaşlanma önleyiciler, koruyucular, şişme ajanları, renklendiriciler ya da özel amaçlar için kullanılan malzemelerdir. Dolgu maddeleri temel olarak; güçlendirici dolgu maddeleri, yarı güçlendirici dolgu maddeleri ya da güçlendirici olmayan dolgu maddeleri olarak üçe ayrılır. Optik özellikler, renk, yüzey özellikleri, yapısal kararlılık, termal, manyetik, elektriksel özellikler, mekanik özellikler, dayanıklılık, reolojik özellikler, kimyasal reaktivite ve biyobozunurluğu etkileyen bir bileşendir. Çoğu kauçuk türü gibi SBR de, güçlendirici dolgu maddesi kullanılmadığı durumlarda çoğu uygulama için uygun değildir. SBR karışımlarında yaygın olarak kullanılan dolgu maddeleri; karbon karası (CB), silika ve killerdir. Kauçuk-kil nanokompozitleri konusu birçok araştırmacı tarafından ilgi görmüş ve günümüzde de ilgi görmektedir. Nano boyutta kil içeren nanokompozitler; gelişmiş mekanik, termal ve gaz bariyeri özelliği, yüksek alev geciktiricilik, çözücü emiliminin daha düşük olması, kimyasal madde ve şekil hafızası gibi özelliklere sahiptir. Haloysit nanotüp (HNTs), son zamanlarda sıkça araştırılan bir malzemedir. Kaolinit grubuna ait bir nanokil türüdür. HNTs'in kimyasal yapısı $Al_2[Si_2O_5(OH)_4].2H_2O$'dur ve topraktan elde edilir. Kompozit malzeme olarak kullanımı çok yaygın değildir ve yeni keşfedilmektedir. İki katmanlı tübüler bir yapıya dahiptir ve kimyasal olarak yapısı kaoline benzer. Silikon dioksit ve aluminium oksit tabakaları arasındaki uyumsuzluktan kaynaklanan gerilimden dolayı tüp şeklini alır. İç yarıçapı 10-30 nm, dış yarıçapı 30-100 nm, uzunluğu ise yaklaşık 10μm'dir. Yüksek L/D oranı, polimerlerin birçok özelliğini geliştirir. Yapılan çalışmalarda, HNTs birçok plastik ve kauçuk için takviye edici ve özellikleri geliştiren bir dolgu maddesi olarak kullanılmıştır. Eşsiz kristal yapıdaki HNTs doğadan mineral olarak elde edilmektedir ve yapı olarak benzeri olan fakat elde edilmesi oldukça pahalı olan karbon nanotüp (CNT)'e bir alternatif olma özelliği taşımaktadır. Ayrıca viskoz bir polimerde dolgu maddesi olarak kullanıldığında, matrikse yapışma problemi olmadığından daha iyi dağılım gösterir ve malzemenin özelliklerini artırır. Doğadan mineral olarak elde edildiği için de ekonomik bir malzemedir. Polimer/kil nanokompozitlerinin performansını belirleyen iki önemli etken arayüz bağlanması ve kilin homojen bir şekilde dağılmasıdır. HNTs aktif olmayan bir yüzeye sahiptir ve kauçuk makromolekülleriyle uyumsuzdur. Bu sebepten istenmeyen arayüz etkileşimlerine sebep olur, kauçuk matrisi içinde topaklanmalar meydana gelebilir ve takviye edici bir dolgu maddesi olarak etkin olamaz. Dolayısıyla HNTs etkin dolgu maddesi olarak kullanılacaksa yüzey modifikasyonu uygulanması gerekir. SBR/HNTs nanokompozitlerinin özelliklerini iyileştirmek için çalışmalar yapılmış ve resorsinol-hegzametilentetramin kompleksi, aminosilanlar, sorbik asit, metakrilik asit gibi bazı modifikasyon ajanları kullanılmıştır. Bunun yanı sıra literatürde kauçuk matrisinde HNTs ve oldukça yaygın şekilde takviye edici dolgu maddesi olarak kullanılan karbon karasının birlikte kullanıldığı çalışmalar da vardır, fakat sayıları sınırlıdır.

Bu çalışmada itakonik asit (IA), çift karboksil grubu ve reaktif asitlerin olumlu etkileri nedeniyle SBR/HNTs ve SBR/HNTs/CB karışımları için modifikasyon ajanı olarak kullanılmış ve etkileri incelenmiştir. 9 adet karışım CB'sız, 6 adet karışım ise CB'lı olmak üzere 15 adet karışım laboratuvar tipi kauçuk milinde hazırlanmıştır. CB'sız karışımlar için HNTs miktarı 0-30 phr aralığında ve IA miktarı 0-5 phr aralığında, CB'lı karışımlarda ise HNTs miktarı 0-20 phr aralığında, IA miktarı 0-1 phr aralığında ve CB miktarı 20-40 phr aralığında tutulmuştur. Karışımların camsı geçiş sıcaklıkları (T_g) ve pişme pik sıcaklıkları diferansiyel taramalı kalorimetre (DSC) ile belirlenmiştir. IA eklenmesi ile pişme pik sıcaklıklarının önemli ölçüde

arttığı gözlemlenmiştir. Karışımların pişme zamanı ve pişme karakteristik özellikleri, 180^{o}C sıcaklıkta, reometre ile belirlenmiştir. Reometre kauçuk karışımının vulkanizasyonu sırasındaki akma davranışını ölçerek reometre eğrisini veren ve kauçuğun pişme karakteristiklerinin değerlendirildiği önemli bir cihazdır. Karışıma istenen yüksek sıcaklık ve basınç altında salınım gerilimi uygular ve çapraz bağ yoğunluğundaki artışın sonucu olarak torktaki artışı zamanın bir fonksiyonu olarak gösterir. Torsiyon reometresi (ODR) ve rotorsuz reometre (MDR) olmak üzere iki çeşit reometre kullanılır. MDR'nin ODR'ye göre üstünlükleri daha fazla olduğu ve kullanım kolaylığı sağladığı için, son zamanlarda reometre cihazı olarak MDR daha yaygındır. Reometre cihazının kaydettiği tork-zaman eğrisi incelendiğinde, testin yapıldığı sıcaklıktaki minimum tork değeri, karışımın minimum viskozitesine (ML) eşittir. %100 pişmenin gerçekleştiği andaki tork değeri MH'tır. Pişmenin ilk başladığı süre hakkında bilgi veren ön pişme (ts2, scorch) süresi ve MH-ML aralığındaki tork değerinin %90'ını elde edebilmek için geçen sürenin %90'ını ifade eden t90 gibi kauçuk malzemenin pişme davranışı hakkında önemli bilgiler veren değerler elde edilmiştir. Karışımların pişme zamanları içerisinde bulunan HNTs, IA ya da CB miktarına gore farklılıklar göstermiştir. Maksimum tork değeri de HNTs, IA ve CB miktarlarından etkilenmiştir; fakat karışımların ML değeri gözle görülür bir değişikliğe uğramamıştır. Pişirmede kullanılan 2 mm'lik kalıpların içini dolduracak karışım kütlesini belirlemek için yoğunlukları ölçülmüştür. Karışımların vulkanizasyon işlemi, 180 ^{o}C sıcaklıkta ve reometrede belirlenen sürelerde, hidrolik preste gerçekleştirildi. 3 adet karışımın (H0/IA5, H20/IA5 ve H30/IA5 karışımları) pişme süreleri 45 dakikayı bulduğundan bu karışımlardan elde edilecek pişmiş örneklerin verimli olmayacağı öngörülmüş ve vulkanizasyon sonrası testler için bu karışımlar kullanılmamıştır. Preste pişirilmiş 2mm kalınlığında hazırlanan plakalardan ASTM D412 standardına gore papyon numuneler kesilmiştir. Kesilen numunelerin mekanik özellikleri (kopma dayanımı, kopmada uzama, elastisite modülü), 500 mm/dk çekme hızıyla gerçeklen çekme testiyle belirlendi. Çekme testiyle elde edilen elastisite modülü değerlerinden ise çaprazbağ yoğunluğu değerleri elde edildi. Nanokompozitlerin çaprazbağ yoğunluğu değerleri HNTs miktarı artışında azalırken, IA varlığı da nanokompozitlerin çaprazbağ yoğunluğu değerlerini olumsuz yönde etkilemiştir. Nanokompozitlerin HNTs, IA ve CB miktarlarına gore kopma dayanımında, kopmada uzama değerlerinde ve elastisite modülü değerlerinde değişiklikler gözlenmiştir. Nanokompozitlerin sertlik değerleri, Shore A tipi durometre ile, ASTM D2240 standardına göre ölçülmüştür. Kauçuk malzemenin sertliği, genel anlamda, metal bir çubuk, bilye ya da iğnenin batmasına karşı gösterdiği direnci ifade eder. Mekanik özelliklerde olduğu gibi sertlik değerleri de nanokompozitlerin HNTs, CB ve IA içeriklerine gore değişiklik göstermiştir. HNTs'nin SBR matrisi içerisinde dağılımı ve nanokompozitlerin morfolojik özellikleri taramalı elektron mikroskobu (SEM) ile belirlenmiştir. SEM fotoğrafları, çekme testiyle koparılmış yüzeyler üzerinden elde edilmiştir. Mikrograflar, nanokompozite IA eklenmesinin, HNTs'nin SBR matrisi içinde dağılımını olumlu yönde etkilediğini göstermektedir. HNTs'nin nanokompozitlerin yanmazlık özelliklerine ekisi, H20/IA1 ve H20/IA1 nanokompozitlerinin sınırlayıcı oksijen indeksi (LOI) değerlerinin ölçümüyle belirlenmiştir. Bu ölçümde kullanılan örnekler, 5cmx10cmx0,6cm ölçülerinde olup, örneklerin hazırlanmasında diğer vulkanizasyon sonrası testler için kullanılan örneklerin hazırlanmasında kullanılan 2 mm'lik kalıp uygun olmamıştır. Elde edilen LOI değerleri, SBR'nin literatürdeki LOI değeriyle karşılaştırılınca, HNTs'in SBR'nin yanmazlık özelliğini geliştirdiği görülmüştür. metoduyla belirlenmiştir.

1. INTRODUCTION

Rubber is a very important class of polymer materials and the production of its nanocomposites by incorporation of nano-fillers has led to the enhancement of its properties significantly and hence expansion of their application potential [1]. Styrene-butadiene rubber (SBR) is a copolymer of styrene and butadiene. It is half of all the synthetic rubber production and is much consumed in tire industry, where it competes with and complements natural rubber (NR) [2,3]. The basic rubber compound formulation insists on raw gum rubber, curing agent, antioxidant, filler and plasticizers. Some popular fillers are, in order of decreasing reinforcement, carbon blacks and silicas, clays and then whitings (calcium carbonate, otherwise known as chalk) [3]. The term 'filler' in rubber technology is often misleading a material that is primarily intended to reduce the cost of the more costly rubber. But the modern-day fillers change one or more of these properties: optical properties and color; improve surface characteristics and dimensional stability; change thermal, magnetic, and electrical properties; improve mechanical properties, durability, and rheology; affect chemical reactivity, biodegradability, etc. Many of the usual applications of elastomers could not be practical without the use of particulate fillers. Widely used fillers for SBR compounds are carbon black (CB), silica and clays [1,3,4]. New-generation nano scaled fillers are challenging the domination of traditional fillers such as carbon blacks and silica in the rubber industry. Nanoscaled fillers such as layered silicates, carbon nanotubes, carbon nanofibers (CNFs), exfoliated graphite, etc. dispersed as a reinforcing phase in an elastomer matrix are emerging as a relatively new form of useful materials. These composites exhibit a change in composition and structure over a nanometer length scale and possess remarkable property enhancements relative to the pure polymer. Owing to the nanometer-sized particles obtained by dispersion, these nanocomposites exhibit superior mechanical, thermal, optical, and dynamic mechanical properties at lower concentrations compared with either the pure polymer or conventional micron-sized composites. Their unique properties stem from a combination of factors such as their high aspect ratio (length to diameter), surface area, and the molecular bonds formed

between the nano-sized filler and the polymer during compounding. Halloysite nanotubes (HNTs) are a nano clay type with large L/D ratio which provides improved properties of polymers. The chemical formula of HNTs is $Al_2[Si_2O_5(OH)_4].2H_2O$. It is similar with kaolinite structure; however HNTs differ from kaolinite with intermolecular water [1,4-14]. It is well known that the dispersion of the filler and the interfacial properties are two important factors on the performance of the polymer composites. HNTs can hardly be effective on reinforcement of rubber because of the unsatisfied interfacial bonding and agglomeration in the rubber matrix without surface modification [8,15,16]. Some studies have been done to improve SBR/HNTs nanocomposites with reactive modifiers e.g sorbic acid and methacrylic acid [15,16]. CB is the most widely used filler for rubber compounds [2] but there are limited studies for HNTs and CB that they were used together as dual filler in literature.

In this study, HNTs was used as filler to enhance properties of SBR. For some compounds. CB was applied as dual filler. HNTs can not be dispersed efficiently and cause agglomerations in SBR matrix. Itaconic acid (IA) considered as a modifier to overcome this challenge with its higher reactivity owing to double carboxylic groups and positive effects of reactive acids. SBR/HNTs compounds were prepared without and with CB at laboratory type two roll mill (HNTs amount was between 0-30 phr and IA amount was between 0-5 phr for compounds which are without CB. HNTs amount was 0-20 phr, IA amount was 0-1 phr and CB amount was 20-40 phr for compounds which are with CB). DSC was used to determine glass transition (T_g) and curing peak (T_p) temperatures of compounds. Curing times and curing characteristics of compounds were examined with moving die rheometer (MDR). Density measurements were done to determine the mass of compounds which will be moulded at hydraulic hot press. The crosslinking process was occurred by hydraulic hot press. Mechanical properties of vulcanizates (tensile strength, elongation at break, Young's modulus) are provided by tensile test machine. Crosslinking densities were procured with Young's modulus values. Hardness values were measured by using a Shore A type durometer. The last experiment for nanocomposites was done with scanning electron microscopy and morphological properties of vulcanizates were determined.

2. THEORETICAL PART

Rubber is a collective term for macromolecular materials. They are a member of substance group like metals, fibers, concrete, wood, plastics or glass. They are different from all other polymeric materials because of their special properties. They are amorphous when unstretched and are above their glass transition temperature while plastics can be crystalline and are used below their glass transition temperature to preserve stability [1].

Originally, the term rubber was used only for the natural product that is obtained from a thick milky fluid called as latex that oozes from certain plants when they are cut. The dictionary definition of rubber is, 'a material that when stretched returns quickly to its approximate original shape'.

Rubber products are used for various applications like tires, hoses, belts, gaskets, elastic bands, electric insulation cables and containers. It is a yellowish, elastic, amorphous material that is obtained from the latex or milky sap of plants like the rubber tree. This latex is a physical mixture of chemicals which includes a lot of ingredients in the vulcanizate might be present only as a physical blend. This latex is vulcanized, pigmented, finished and modified into rubber products [2,3].

2.1 The History of Rubber

It is founded that the Aztecs and Mayas of South America, who used rubber for shoe soles, coated fabrics, and play balls, well over 2,000 years ago.

Christopher Columbus as the first European to discover NR, in the early 1490s, when he found natives in Haiti playing ball with an extract from a tree.

Scotsman Macintosh used the solvent naphtha to decompose rubber and applied the resulting solution to textiles to produce rainproof clothing in 1823.

Thomas Hancock in London in 1830 used what the first internal mixing machine, which mechanically worked the rubber, decreasing its viscosity and hence it is easier to mix it. Then, Hancock used two roll mills to prepare rubber compounds.

There was a problem for rubber products up to the 19th century. They were sticky at high temparatures and brittle when cold. This problem was solved in 1839 by an invention which belongs to Charles Goodyear. Goodyear accidentally visited the rubber goods store of the Roxbury Company in New York, in 1832, and as a result became compulsive about this problem. In his search to make it more useful, he purchased the claim of combining sulfur with rubber. Then, Goodyear was responsible for US Government to produce mail bags. These bags were made from rubber which included sulfur and white lead. The mail bags started to disintegrate in a short time. By chance he heated the raw rubber-sulfur-lead mixing and vulcanized was born. The resulting composition was a much stronger material and was no longer sticky at higher temperatures. Goodyear took a US patent for this important invention in 1841.

In 1889 John Dunlop discovered the first commercially successful pneumatic tire, which used for bicycles. Dunlop manufactured his first vehicle pneumatic tire in 1906. In 1904, in England, CB was found, compounded into rubber, considerably increased its properties.

The Russians, made such a rubber chemically as polybutadiene (BR). In the 1930s, the Germans began to industrial production of a synthetic rubber called Buna-S (styrene butadiene copolymer). Beginning from Second World War, a lot of R&D project was initiated, between government and industry in the United States. Styrene butadiene rubber was improved, then manufactured on a large scale and called Government Rubber-Styrene (GR-S), later to be known generically as SBR, which today is a major material in the rubber industry [3].

2.2 Types of Rubber

Rubbers are divided into two groups as natural rubber and synthetic rubbers. The basic material for a rubber compound is raw gum rubber. The other ingredients are curing agents, filler, antioxidants, plasticizer, etc. [3].

2.2.1 Natural rubber (NR)

NR is a linear, long chain polymer known as cis-1,4 polyisoprene. The chemical structure of polyisoprene can be seen from Figure 2.1.

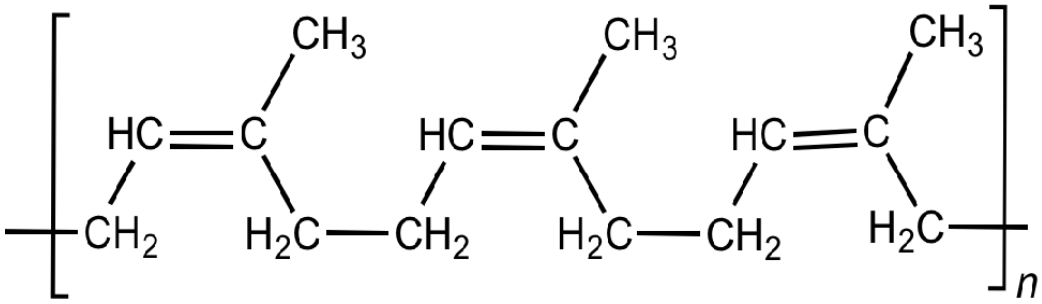


Figure 2.1 : Chemical structure of cis-1, 4 polyisoprene.

Obtaining of NR begins at the plantation where a slit is made into the bark of the rubber tree to allow the flow of a milky resin (Figure 2.2). This latex includes water, polyisoprene, and small quantities of other ingredients such as proteins and carbohydrates. It is collected and coagulated with formic acid in large tanks.

Figure 2.2 : Tapping latex from a rubber tree.

Properties of materials which made from NR;

- Good mechanical properties and excellent elasticity,
- Relatively low cost and good abrasion resistance make it a convenient material to produce slurry pump liners, impellers and tank linings.

- Good dynamic mechanical properties. Therefore used in tires, rubber springs and vibration mounts.

It also has very good low temperature resistance, down into the region of -57 ^{o}C at which its stiffness shows a considerable increase. Electrical insulation is very good and, like all elastomers, is dependent on compounding. Dilute mineral acid (although not oxidizing acids such as nitric) and dilute base resistance is good. Solvents follow the polarity rule, thus resistance to petroleum oils is poor while resistance to alcohols (such as ethanol and methanol) and ketones (such as methyl ethyl ketone (MEK) and acetone) is much better [3]. General properties of NR are summarized at Table 2.1.

Table 2.1 : Properties of natural rubber before and after vulcanization [17].

Property	**Raw Rubber**	**Vulcanized Rubber**	**Reinforced Rubber**
Tensile Strength (MPa)	2.1	20.1	31
Elongation at Break (%)	1200	800	600
Modulus (MPa)	-	2.7	17.2
Permanent Set	Large	Small	
Rapidity of Retraction (snap)	Good	Very Good	
Water Absorption	Large	Small	
Solvent Resistance (Hydrocarbons)	Soluble	Swells Only	

2.2.2 Synthetic rubbers

They include rubbers which are butadiene rubber (BR), polyisoprene rubber (IR), butyl rubber (IIR), ethylene-propylene-diene rubber (EPDM), acrylonitrile-butadiene rubber (NBR), polychloroprene (CR) and styrene-butadiene rubber (SBR). Some of them are using for special purposes like silicone rubber, floroelastomer rubber (FKM), ethylene-vinyl acetate copolymer (EVA), polyacrylate rubbers (ACM) etc [17, 18]. Most used one (silicone rubber) is explained at section 2.2.2.7. below detailed. General synthetic rubber production system and some properties of common rubbers can be seen from Figure 2.3 and Table 2.2 respectively.

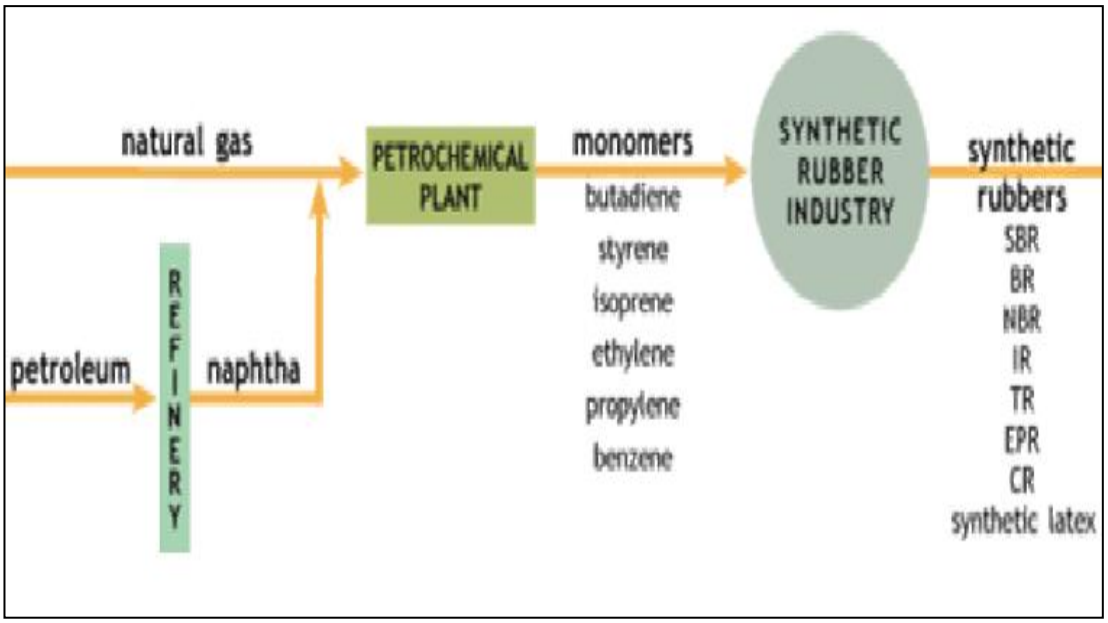


Figure 2.3 : Main synthetic rubber production system [19].

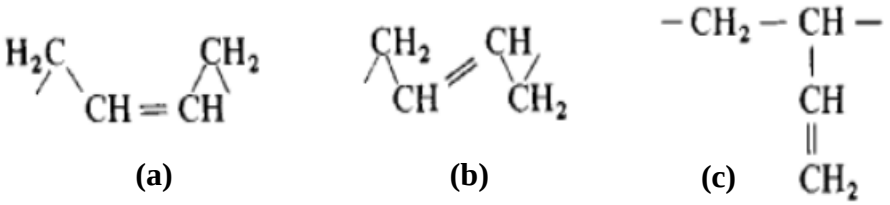
Table 2.2 : Some properties of common rubbers [17].

Rubber	Maximum Tensile Strength (MPa)	Brittle Point (^oC)	Minimum Hardness (Shore A)	Maximum Hardness (Shore A)
IR	13.8	-58	30	90
BR	13.8	-73	40	80
NBR	17.2	-51	40	90
EPDM	13.8	-58	40	90
CR	17.2	-54	40	90
IIR	13.8	-58	40	80
FKM	13.8	-40	55	90

2.2.2.1 Polybutadiene rubber (BR)

BR is a homopolymer of 1,3 butadiene, a monomer containing four carbon atoms, and six hydrogen atoms (C_4H_6) [19]. Like isoprene, BR can be synthesized anionically or via Ziegler-Natta catalysis. Cold emulsion BR is also available [18,19].

There are 3 different types of BR in literature depending on their obtaining reaction. These are cis -1,4 polybutadiene, trans-1,4 polybutadiene and 1,2-vinyl polybutadiene. The chemical structure of these rubbers can be seen in Figure 2.4.



(a) **(b)** **(c)**

Figure 2.4 : The chemical structures of possible BR **(a)** Cis -1,4 polybutadiene; **(b)** Trans - 1,4 polybutadiene; **(c)** 1,2 Vinyl polybutadiene.

High cis 1,4 polymers have a T_g around -90 ^oC, so they show good low temperature flexibility. Also they exhibit excellent resilience and abrasion resistance. On the other hand, the high resilience gives poor wet grip in tire treads.

As the cis 1,4 content decreases, and 1,2 vinyl content increases, the low temperature properties, abrasion resistance and resilience become inferior.

Mostly BR is used in tire applications. So it is an important component for NR and SBR blends. The friction on ice of winter tires is also improved by using higher contents of BR in the tire blends. Shoes, conveyor and transmission belts are the other applications of BR [20].

2.2.2.2 Polyisoprene rubber (IR)

IR is obtained anionic or Ziegler-Natta polymerization. The former material has up to 95% cis-1,4 microstructure, while the latter may be as much as 98% stereoregular. The difference in stereoregularity is small but Ziegler-Natta IR is substantially more crystallizable [18]. The possible configurations of IR are shown in Figure 2.5.

Although similar to NR, IR shows some differences:

- Compounds of IR have lower modulus and higher elongation at break values.
- It is more uniform and lighter in color.
- It exhibits less of a tendency to strain crystallize, hence green strength is inferior, as are both tensile and tear strengt [18, 20].

It can be applied instead of NR. It is used in blend with BR and SBR, especially processibility improvement is required [20].

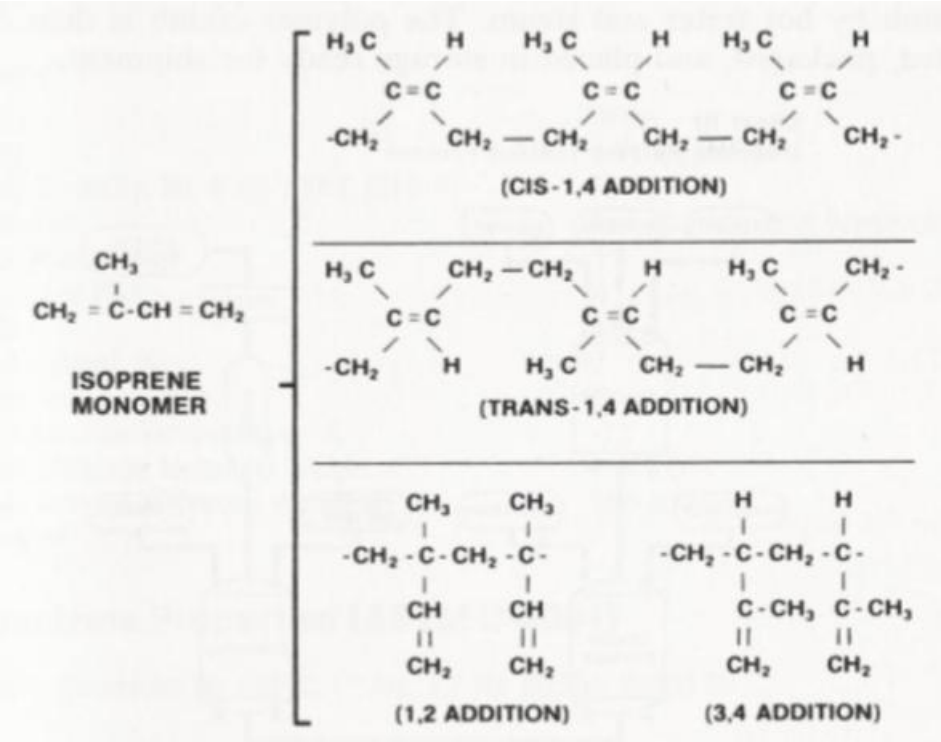


Figure 2.5: Possible IR configurations [21].

2.2.2.3 Butyl rubber (IIR)

IIR is a copolymer of isobutylene with a small percentage of isoprene. The chemical structure of IIR can be seen from Figure 2.6. Isoprene content affects the curing rate and resistance of the rubber to oxygen, ozone and ultra violet (UV) light [20,21].

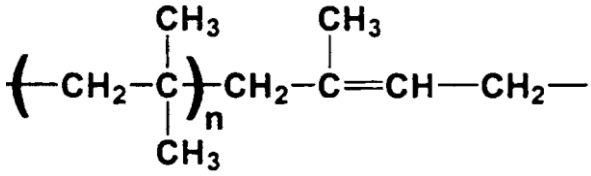


Figure 2.6 : Chemical structure of IIR.

IIR has unusually low resilience for an elastomer with such a low T_g (about -70 ^oC).

IIR has excellent aging stability however permeability to gases is low. Thus, it is widely used in inner tubes and tire innerliners. The other applications are wire and cable production, pharmaceutical closures and vibration isolation.

Brominated (BIIR) and chlorinated (CIIR) modifications of IIR are also available [20].

2.2.2.4 Ethylene-Propylene-Diene Rubber (EPDM)

EPDM is a non-polar hydrocarbon based elastomers including ethylene and propylene units in the main chain [22]. The chemical structure of EPDM is can be seen from Figure 2.7.

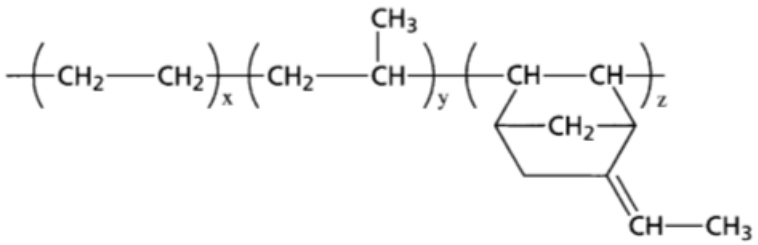


Figure 2.7 : Chemical structure of EPDM rubber.

Vulcanizates of EPDM elastomers are extremely resistant to attack by ozone, oxygen and weather [7]. On the other hand, they have good heat resistance (their application can rise to 148-176 ^{o}C). Also they can be appropriate about at -50 ^{o}C. Because of their mechanical properties, EPDM rubbers have good resistance to impact and abrasion.

EPDM rubbers are used in the automobile industry, cable insulation, power plants, plastic modification, weather protection, roof system applications and the electrical industry [22].

2.2.2.5 Acrylonitrile-butadiene rubber (NBR)

NBR, also termed nitrile rubber, is an emulsion copolymer of acrylonitrile and butadiene. Acrylonitrile content varies from 18 to 50% [19]. Structure of NBR is shown in Figure 2.8. Many properties (oil resistance, tensile strength, hardness, abrasion resistance etc.) of NBR enhances with acrylonitrile content increment [20].

NBR is widely used in sealing applications, hose liners, roll coverings, conveyor belts, shoe soles and plan linings due to its higher oil resistance [17].

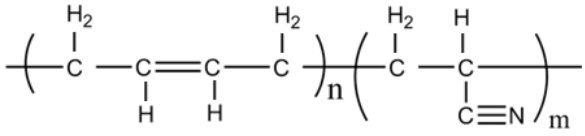


Figure 2.8 : Chemical structure of NBR.

2.2.2.6 Polychlorprene (CR)

CR is obtained by emulsion polymerization of 2-chlorobutadiene and has a T_g of about, -50 ^oC [18].

The possible additions for CR can be seen from Figure 2.9 [20].

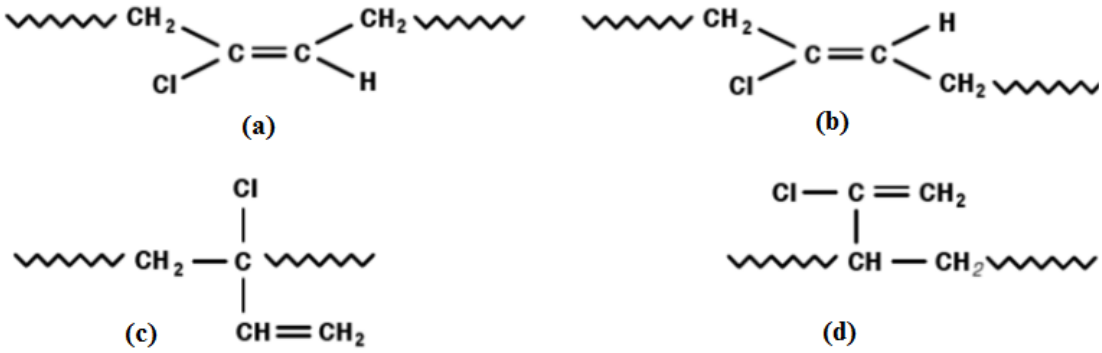


Figure 2.9 : Possible additions for CR **(a)** Cis-1,4 addition, **(b)** Trans-1,4 addition, **(c)** 1,2 addition, **(d)** 3,4 addition.

2.2.2.7 Silicone rubbers (Q)

Most silicone rubbers have the repeat unit empirical formula of $((CH_3)_2SiO)$ and are referred to as polydimethylsiloxanes as can be seen from Figure 2.10. The elastomer consists of alternating silicon and oxygen atoms with two methyl groups on each silicon. A significant departure from most other elastomers is the absence of carbon in the backbone. Three reaction types are predominantly employed for the formation of vulcanised Q: peroxide-induced free-radical vulcanisation, hydrosilylation addition cure, and condensation cure. Silicones have also been cross-linked using radiation to produce free radicals or to induce photoinitiated reactions [20, 23].

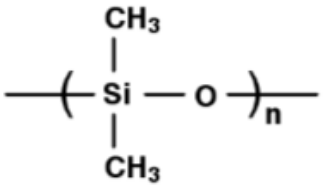


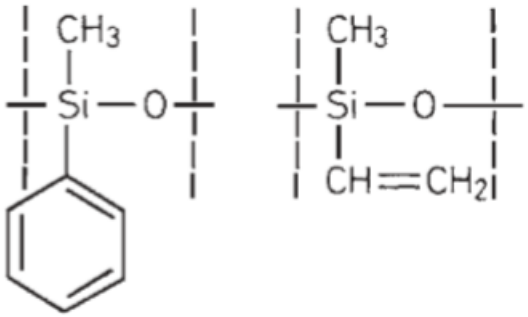
Figure 2.10 : Chemical structure of polydimethylsiloxane.

Polymers which just contain methyl silicones are termed as MQ. It is possible to obtain by replacing with a vinyl group instead of the methyl groups (<0.5%). The

result rubber is named as vinyl methyl silicone (VMQ). It shows enhanced vulcanization characteristics and lower compression set.

Phenyl modified silicones (PMQ or PVMQ) are obtained by using 5-10% phenyl groups instead of methyl groups. They have better low temperature properties compared with VMQ. Figure 2.11 shows those chemical structures of PMQ and WMQ, respectively.

Silicone rubbers are used in medical, wire, cable, automotive and aerospace applications [20].



(a) **(b)**

Figure 2.11 : Chemical structure of **(a)** PMQ **(b)** VMQ.

2.2.2.8 Styrene-butadiene rubber (SBR)

During 2nd World War, the suppliers interrupted the NR thus USA and Germany found another solution, synthesised SBR [20,21].

SBR is a copolymer of styrene and butadiene. The chemical structure of SBR can be seen from Figure 2.12.

It mainly provided from emulsion or solution polymerization (E-SBR or S-SBR) [24]. The property differences between E-SBR and S-SBR are signed in Table 2.3.

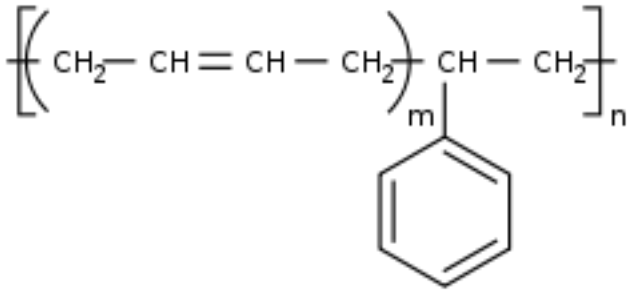


Figure 2.12 Chemical structure of SBR.

Table 2.3 : Properties of E-SBR and S-SBR [24].

	E-SBR	**S-SBR**
Styrene Content (%)	23-40	18-25
Vinyl Content (%)	15-20	10-80
Styrene Dispersion	Random	Block or random
Moleculer Weight (MW)	Not Contollable	Controllable
MW Distribution	Broad	Narrow
Long Chain Branching	Substantially	Low

SBR constitutes half of the synthetic rubber production and is much consumed in tire industry, where it competes with and complements NR [3].

SBR can be met in almost all sectors of the rubber industry. Used mainly for tires, often in blends with NR; conveyor and conveyor belts, footwear soles and heels; technical goods of all kinds, for example, seals, membranes, hose, and rolls [25]. Some SBR types and their applications are shown at Table 2.4.

Table 2.4 : Some SBR types and their application areas [22].

Type	**Application Area**
SBR 1500	Tread rubber, technical rubbery materials
SBR 1502	Tehnical material which has lighter colour
SBR 1507	Materials which are used in extrusion or calender
SBR 1509	Cable and electrical goods
SBR 1516	Extruded materials with shining surfaces (Higher styrene content
SBR 1573	Clutch/Brake linings, adhesives
SBR 1707	Hoses, profiles, shoes, flooring
SBR 1712	Tread rubber, conveyor belts
SBR 1778	Lighter colour or transparent technical rubbery materials, flooring
SBR 1618	Technical rubbery materials, extruded materials
SBR 1803	Tread rubber, electrical materials
SBR 1843	V-belts

- **Properties of SBR**

SBR has lower mechanical properties when it is compared with NR and CR. The chemical, solvent and weather resistance properties of SBR are similar to NR The upper temperature limit for heat aging resistance is a slightly higher [3]. When

fotoelectrical insulation properties are considered, it is similar with NR. General properties of SBR are summarized in Table 2.5.

Table 2.5 : General properties of SBR [22].

Spesific gravity (g/cm^3)	0.94
Tensile strength (MPa)	>21
Hardness (Shore A)	40-100
Elasticity	Good
Tear strength	Good
Abrasion strength	Excellent
Compression set	Medium-Good
Atmospheric aging resistance	Poor-Good
Oxidizing strength	Good
Heat endurance	Good
Lower temperature endurance	Good
Moisture endurance	Good
Gas permeability	Medium
Endurance for aqueous acid	Medium-Good
Endurance for concantrated acid	Medium
Endurance for hydrocarbons	Poor
Endurance for oils and fuels	Poor
Endurance for vegetable or animal oil	Poor-Good
Dielectric Properties	Good

- **Blending with other rubbers**

SBR is a nonpolar dien rubber. It can be easily blended with other nonpolar rubbers. SBR-NR or SBR-BR blends are important for especially tire and shoe manufacturing. Blending with BR is enhanced the abrasion strength, wearing resistance and elasticity at lower temparature of compound. Blending with NR improves the abrasion and tearing properties. In cases which oil resistance is a necessity; it can be blended SBR with NBR. Mixing with EPDM and IIR is inadvisable [22].

The global consumption of SBR in 2012 is shown in Figure 2.13.

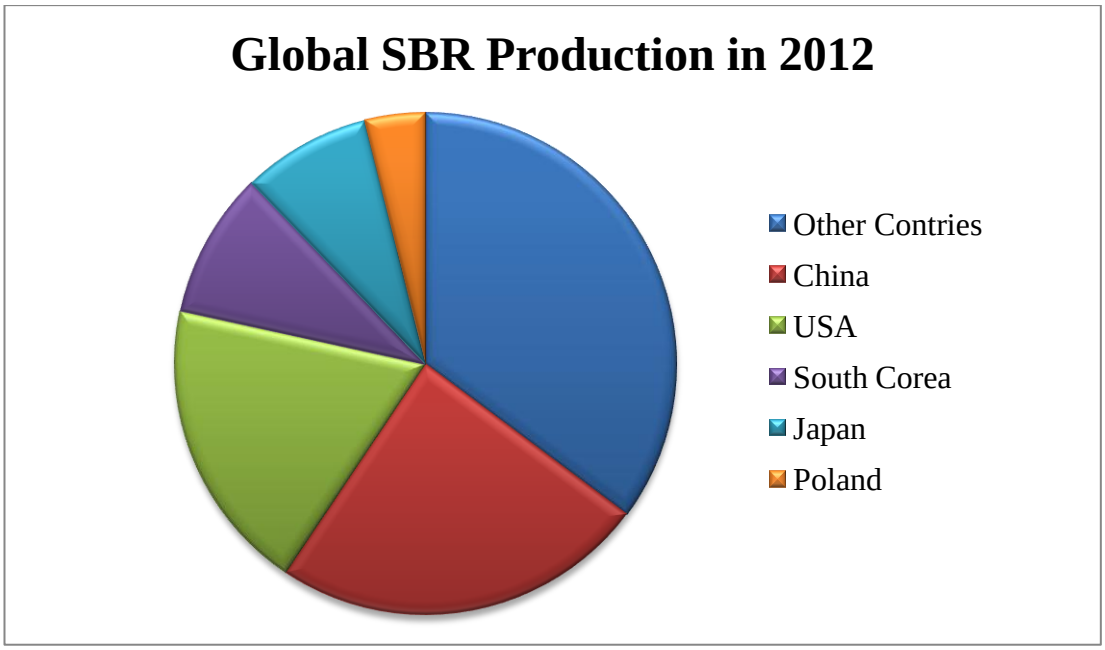


Figure 2.13 : Global SBR production in 2012 [26].

It is not possible to produce CR commercially which has cis 1,4 chemical structure. Common CRs are based on trans 1,4 form. It has a melting point, T_m, of 75 ^oC and a T_g of -45 ^oC [20].

Compared to BR, NR, IR and SBR elastomers, CR has superior weatherability, heat resistance, flame resistance, and adhesion to polar substrates, such as metals. In addition, CR has lower permeability to air and water [18].

2.3 The Basic Rubber Compounds

The rubber compound is adjusted to desired properties with rubber and additives which can be vulcanized.

Desired properties from a rubber compounds;

- Desired properties from finishing properties,
- Convenience for used machines and process,
- Cost convenience for competition

Substances which are used in a rubber compound;

- Rubber
- Vulcanization substances

    - Curing agent
    - Accelerators
    - Activators
    - Retardants
- Reinforcing or non-reinforcing fillers
- Plasticizers
- Process facilitators
- Anti-agings and protectors
- Blowing agents
- Colorings
- Substances for special purposes

The common specialty for each rubber compounds is having a rubber and vulcanization system. Elasticity cannot occur without them. The other ingredients are optional for obtaining various properties for end products.

The rubber formulation (recipe) is prepared considering rubber as 100 units. The other component are defined in part per hundred rubber (phr) amount [22]. A general rubber recipe is listed at Table 2.6.

Table 2.6 : A general rubber recipe [3].

Material	**Amount (phr)**
Raw gum elastomer	100
Curing agent	0-4
Activator	5
Process facilitator	2
Accelerator	0.5-3
Antioxidant	1-3
Filler	0-150
Plasticizer	0-150

2.3.1 Vulcanization

Vulcanization or crosslinking (curing) is a chemical reaction for converting rubber into more durable materials via the addition curing agents. Vulcanization also reduces the effects of heat or solvents on the properties of a rubber compound and to obtain useful mechanical properties. Unvulcanized rubber is generally not very strong, does not sustain its shape after a deformation, and may be very sticky [3,27,28]. In Figure 2.14, the vulcanizate properties are shown as a function of crosslinking density.

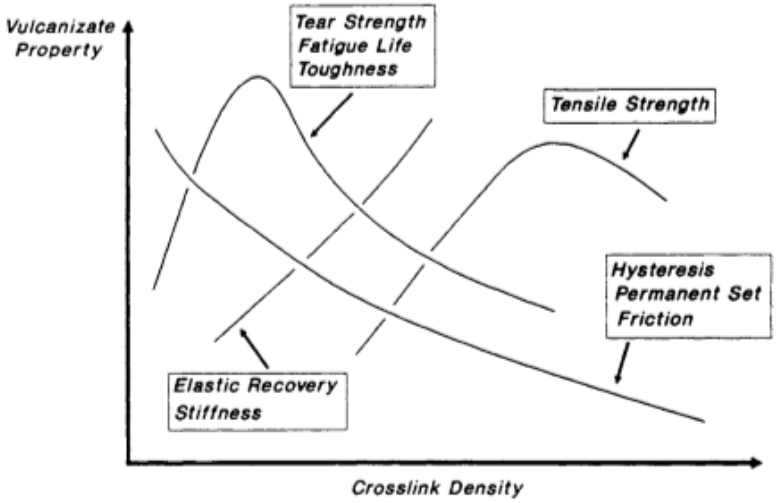


Figure 2.14 : Vulcanizate properties as a function of the extent of vulcanization [28].

During vulcanization process, by locking chain each other with the vulcanization agent to form three-dimensional structure. This reaction transforms the soft, weak plastic-like material into a strong elastic and more dimensionally stable product. The structural differences between unvulcanized rubber and vulcanized rubber are shown in Figure 2.15. Sulfur and peroxide, are the most widely used (95% of all curing systems) crosslinking agents. In sulfur vulcanization systems activators and accelerators must be used. The other ways of crosslinking are resin curing, metaloxide curing, ultraviolet curing and radiation curing.

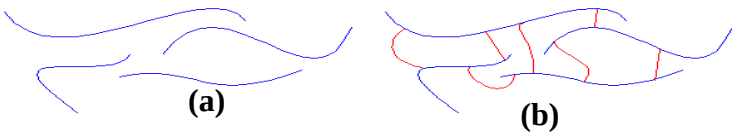


Figure 2.15 : The structural differences of **(a)** Unvulcanized rubber, **(b)** Vulcanized rubber.

2.3.1.1 Sulfur vulcanization

Sulfur is the most widely used vulcanizing agent in combination with activators and accelerators. It reacts chemically with unsaturated parts to create cross-links between two or more polymer chains, resulting in a more dimensionally stable and more heat resistance product. It is a very complex reaction and involves activators for the breakage of the sulfur ring (S_8) and accelerators for the formation of sulfur intermediates, which facilitate sulfur-to-double bond crosslinkings [3,27-29]. Crosslinking of IR with sulfur can be seen in Figure 2.16.

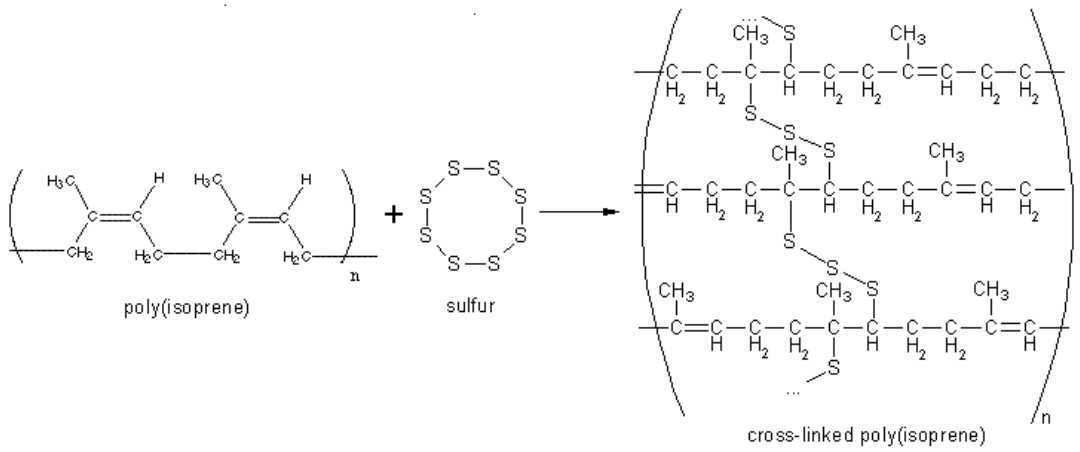


Figure 2.16 : Crosslinking of IR with sulfur [30].

- **Activators**

Zinc oxide and stearic acid, together with sulfur and accelerator, constitute the 'cure system' for the formulation. Zinc oxide reacts with stearic acid to form zinc stearate (in some cases zinc stearate is used in place of zinc oxide and stearic acid) and together with the accelerator they speed up the rate at which sulfur vulcanization occurs. With sulfur alone, the curing process might take hours. With activator using curing system, vulcanization can be reduced to minutes [3].

- **Accelerators**

Organic chemical accelerators were not used until 1906 (65 years after the Goodyear-Hancock development of unaccelerated vulcanization) when the effect of aniline on sulfur vulcanization was discovered by Oenslager [28].

Accelerators are usually organic materials, and they speed up the rate of vulcanization. There are many accelerators available and they can be classified into several chemical classes as can be seen from Figure 2.17.

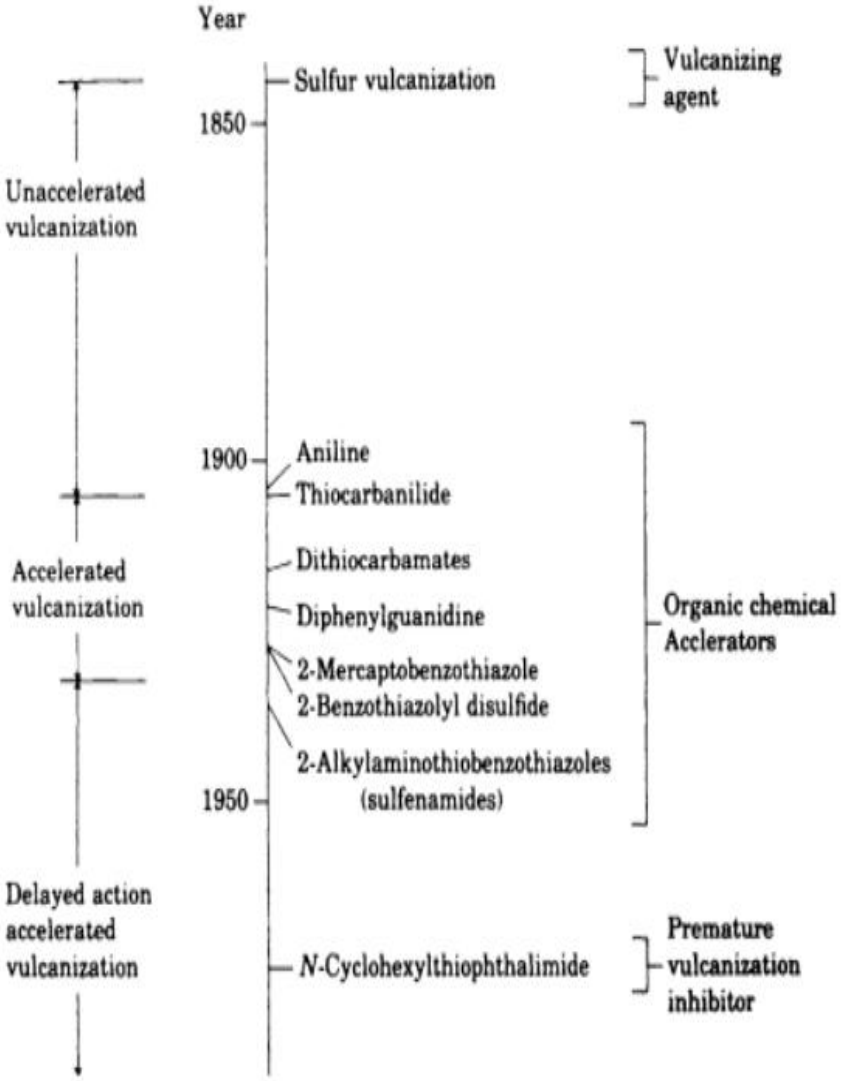


Figure 2.17 : The history of accelerators [28].

It is the only rapid crosslinking technique that can, in a practical manner, give the accelerated action required for processing, shaping, and forming before the formation of the compelling vulcanized network.

Some accelerators are able to provide sulfur from their own chemical structure. Thus the need for elemental sulfur might be reduced or eliminated in the recipe. They are called sulfur donors (for example tetramethylthiuram disulfide (TMTD)). Accelerators are used to vulcanize NR, IR, SBR, NBR, IIR, CIIR, BIIR, and EPDM

[28, 29]. Basic mechanism of accelerated sulfur vulcanization can be seen from Figure 2.18.

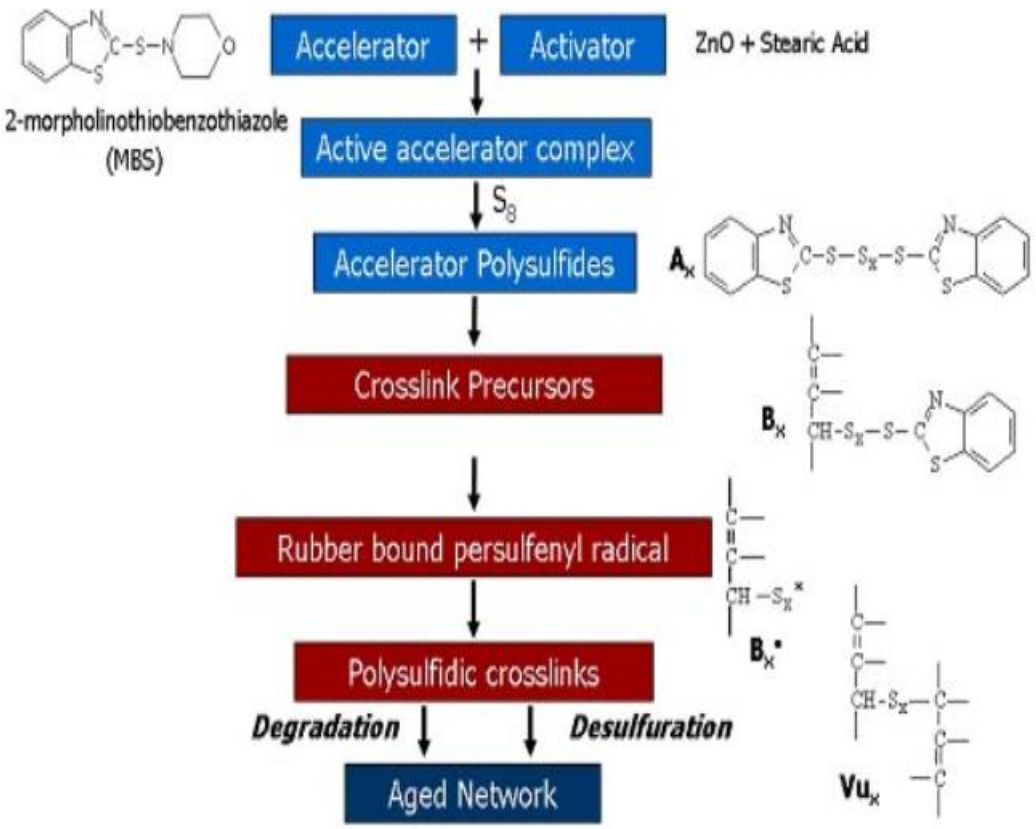


Figure 2.18 : Basic mechanism of accelerated sulfur vulcanization [31].

2.3.1.2 Peroxide vulcanization

The saturated rubbers cannot be cured by sulfur and accelerators. Organic peroxides are necessary for the vulcanization of these rubbers. The production of free radicals is the driving force for peroxide crosslinking [9]. Diacyl peroxides, dialkyl peroxides, and peresters have been used. Dialkyl peroxides and t-butyl perbenzoate give efficient crosslinking. Di-t-butyl peroxide and dicumyl peroxide give good vulcanizates, but the former is too volatile for general use. Dicumyl peroxide is widely used, however its vulcanizates have the odor of acetophenone, which is a byproduct of the vulcanization process [28].

Crosslinking systems based on peroxides are usually simple. Unlike with sulfur vulcanization systems, the addition of ZnO and stearic acid is not necessary. Thus crosslinking is achieved simply using peroxide [29].

2.3.2 Fillers

The reinforcement of elastomers by particulate fillers has been extensively studied in the past, particularly in the 1960s and 1970s. The first reason is naturally the important changes in mechanical properties with fillers reinforcement: many of the usual applications of elastomers could not be practical without the use of particulate fillers. It is necessary to define the reinforcement, because this word has different meanings when applied to thermoplastics, thermosets, or elastomers. For plastics, reinforcement results an increment in modulus and hardness. The effect of particulate fillers is quite clear; they replace a part of the matrix: so modulus becomes higher, but deformation at break decreases in the same time. For elastomers; it is occurred an increment for modulus by reinforcing fillers. The replacement of a part of the matrix by solid objects does not reduce its deformability [32].

2.3.2.1 Carbon black (CB)

CB ise second only to rubber as the most critical and widely used raw material of the rubber industry. It is principally made by incomplete combustion of heavy petroleum products and small amounts from vegetable oils. CB consists of extremely small particles (from around 10 to 300 nm) in a grape- like aggregate. Scanning tunneling microscopy observation of CB surface is shown at Figure 2.19. This gives two primary properties allowing a whole range of grades designated by both a particular particle size (surface area) and a specific level of structure.

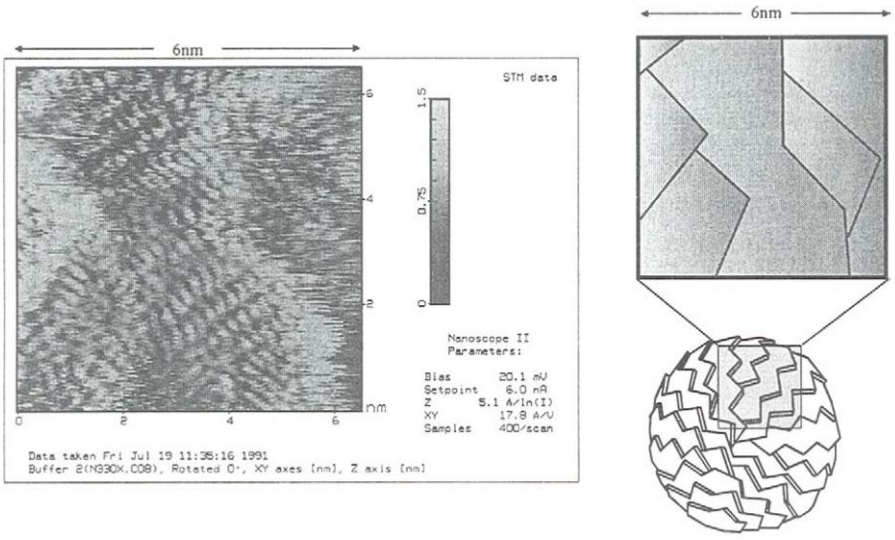


Figure 2.19 : Scanning tunneling microscopy observation of CB surface at atomic scale resolution [32].

A decrease in carbon black particle size (increase in overall surface area to volume ratio) increases the tensile strength of the cured vulcanizate. Very fine particle size is difficult to disperse adequately and when dispersion is achieved give a high reinforcement. Although large particle size blacks are easily completely dispersed, they do not give reinforcement. CB is also a powerful UV absorber and will give a measure of protection against sunlight to the rubber [3,29]. The relationship between particle size of CB and property value of rubber can be seen from Figure 2.20.

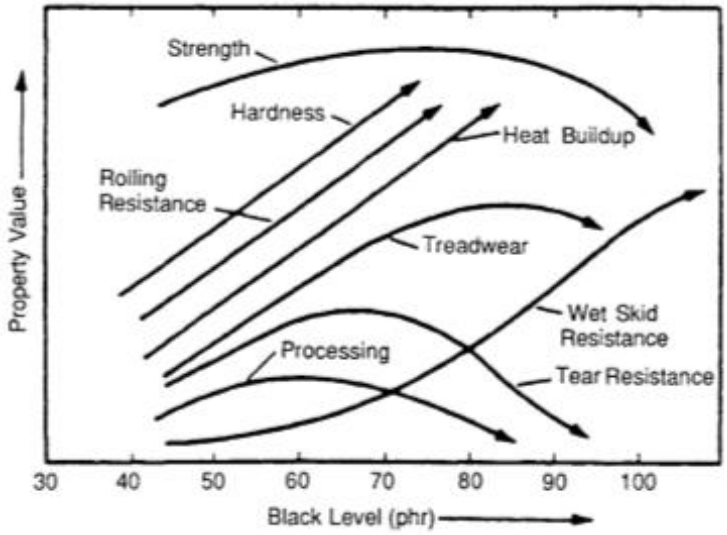


Figure 2.20 : Effect of CB level on compound properties [32].

2.3.2.2 Silica

Second widely used reinforcing fillers are silicas after CB [33]. The use of silica in rubber compounds cannot be considered as new filler, because it has been used in rubber formulations since the beginning of the 20th century [32]. Addition of silica to a rubber compound offers a number of advantages such as improvement in tear strength, reduction in heat build-up, and increase in compound adhesion in multi component products such as tires. Two fundamental properties of silica and silicates influence their use in rubber com- pounds: ultimate particle size and the extent of hydration. Other physical properties such as pH, chemical composition, and oil absorption are of secondary importance. Silicas, when compared to carbon blacks of the same particle size, do not provide the same level of reinforcement, though the deficiency of silica largely disappears when coupling agents are used with silica [32]. Its particle sizes are in the range of 10-40 μm. The silica has a chemically bound water content of 25% with an additional level of 4-6% of adsorbed water. The

surface of silica is strongly polar and the hydroxyl groups bound to the surface of the silica particles [29].

Silica fillers offered to the rubber industry are of three specific types;

• Ground mineral silica,

• Precipitated silica, and

• Fumed or pyrogenic silica.

- **Ground mineral silica**

Ground silica, generally available below 47μm, is used as cheap heat resistant filler for a variety of compounds. There is no effect on the rate or state of cure [29].

- **Precipitated silica**

Silica used as reinforcing fillers is mainly obtained by precipitation. The process basically consists in the preparation of a silica glass by alkaline fusion of pure sand and an alkaline salt. Then this glass is solubilized in water at high temperature and acid precipitated. The silica suspension obtained is then filtered, washed, and dried [29].

- **Fumed silica**

They are obtained by high temperature oxydecomposition of SiH_4, or other methyl hydride precursors ($SiHMe_3$, SiH_2Me_2,etc.):

$$n\ SiH_4 + 2n\ O_2 \rightarrow n\ SiO_2 + 2n\ H_2O$$

Coming out of the furnace, fumed silicas are obtained in a fluffy form, and because of their high temperature of formation, they present a very stable morphology and few surface silanols compared to precipitation silicas. This confers a high dispersibility and reactivity to fumed silicas but, because of their higher price, they are rarely used in the rubber industry [32].

Although silica is more expensive than carbon black, there is a huge supply of the raw material in nature [3].

2.3.2.3 Other fillers

At the other end of the reinforcement scale is ground calcium carbonate (known as chalk, limestone or whiting to the rubber compounder). The ground material is used as low cost filler with no reinforcing effect. In its precipitated form it has some reinforcing ability. Another group of fillers are the clays which are naturally occurring hydrated aluminum silicates. The grades available are lower in cost than silica and reflect a choice of reinforcement (soft or hard). The soft clays have some reinforcing properties and larger quantities (than hard clay), a few hundred phr, can be added to a rubber compound. The hard clays confer a distinctly improved level of reinforcement than the softer version. Hard clay can be calcined (heated to remove water) to produce a product with superior electrical (insulating) properties. Organic chemicals, added as a surface treatment to the filler, can improve some properties. Other fillers available are aluminum hydroxide, coal dust, lignin, silicates and talc [3]. HNTs clay which is used this study is explained in detail at section 2.5.1.

2.3.3 Plasticizers

Oils and other slippery materials are called plasticizers. ASTM D 1566 defines them as ‘a compounding material used to enhance the deformability of a polymeric material’. Their function at low levels is to aid in the dispersion of fillers. At higher amounts they reduce uncured compound viscosity, lower compound cost, reduce vulcanizate stiffness and in some cases improve low temperature flexibility. They also improve flow in extrusion and molding by making the uncured compound less elastic and reducing viscosity and friction. Petroleum oils are one of the major sources of plasticizers for rubber compounds. These oils are divided into three chemical categories; aromatic, naphthenic and paraffinic [29]

2.3.4 Other ingredients

2.3.4.1 Antioxidants

The term antioxidants refer only to products that inhibit the effects of oxygen. Antioxidants are used to protect rubbers from the effects of thermal oxidation. Peroxide vulcanizates are usually protected with dihydroquinolines. Other antioxidants react with the peroxide inhibiting the crosslinking reaction [29].

2.3.4.2 Antiozonants

Ozone attack on rubbers takes the form of cracking which takes place perpendicular to the direction of the strain. Ozone attack occurs mainly at the olefinic double bond of a diene rubber. If they are not protected against ozone, the result will be loss of physical integrity for thin sectioned articles and surface cracking on larger mass products. Excess dosage of antiozonant can result in the formation of unsightly blooms on the rubber surface. Using fewer antiozonant can lead to worse attack than when none is present [29].

2.3.4.3 Process additives

Rubbers are difficult to process at some stage during their manufacturing. Some rubbers are tough materials which are difficult to mix with the compounding ingredients. Other rubbers have a great affinity to the metal of the mixer chamber and rotors and are difficult to remove after being compounded. A process additive is an ingredient which is added in a small dosage to a rubber compound to influence the performance of the compound in factory processes, or to enhance physical properties by aiding filler dispersion. The process additive should ideally:

- Aid dispersion,
- Reduce polymer tense,
- Promote compound flow characteristics,
- Act at a low dosage level,
- Not adversely affect the finished product,
- Reduce power consumption [29]

Process additives can be classified as dispersives, viscosity enhancing materials, peptizers, stickiness enhancing materials and plasticizers for special purposes [33].

2.3.4.4 Pigments

A relatively small proportion of colored rubber products are produced. When colored products are produced, white fillers are used. These are a good base white pigmentation as a foundation for the color of the product. Correct color matching is very hard in rubber industry. Matching the color of the un-vulcanized compound to a given standard color may not be sufficient. Pigments change color to a minor or

major extent when subjected to heat and to protective and vulcanization ingredients in the compound [29].

2.3.4.5 Antistatic agents

The production of light colored products with a requirement for low build-up of static electricity requires the addition of an ingredient which is capable of providing the rubber with a low electrical resistance [29].

2.3.4.6 Fire retardants

The majority of rubbers support combustion. The by-products of the combustion can be lethal. In order to improve the resistance of the rubbers which support combustion, a number of products may be added to the rubber compound. These may be inorganic or organic in nature [29].

2.3.4.7 Prevulcanization inhibitors

Sulfur vulcanization of rubber is catalyzed by the presence of alkali materials. This activation of the vulcanization system can result in unwanted short scorch times. The addition of weak acids to the rubber compound results in retardation of the crosslinking mechanism [29].

2.4 Rubber Compounding

Mixing or compounding is accomplished using mills and/or internal mixing machines. The resulting compound is then preshaped by mills, extruders or calenders, to prepare it for vulcanization.

2.4.1 Mills

These were used at the beginning of the rubber industry and are still an important piece of rubber processing equipment.

A mill consists of two horizontally placed hollow metal cylinders rotating towards each other as can be seen from Figure 2.21. The distance between the cylinders (mill rolls) can be varied, typically between 0.25 to 2.0 cm. This gap between the rolls is called a nip [3].

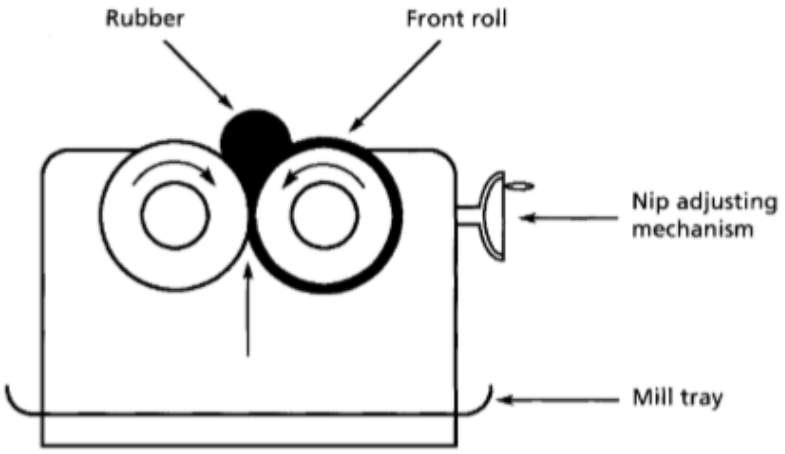


Figure 2.21 : Conceptual view of rubber mill rolls [3].

2.4.2 Internal mixing machines (Banbury)

The internal mixer rapidly became an essential part of the rubber industry. They are capable of mixing a kg or so, to those that can mix more than 500 kg per load, equivalent to many large mills. The internal mixer is faster, cleaner, (produces less dust from powdery materials such as carbon black, silica and clay), uses less floor space, and is probably less operator sensitive. It has thus displaced the mill for most compounding operations [3]. The conceptual cross-sections through banbury can be seen at Figure 2.22.

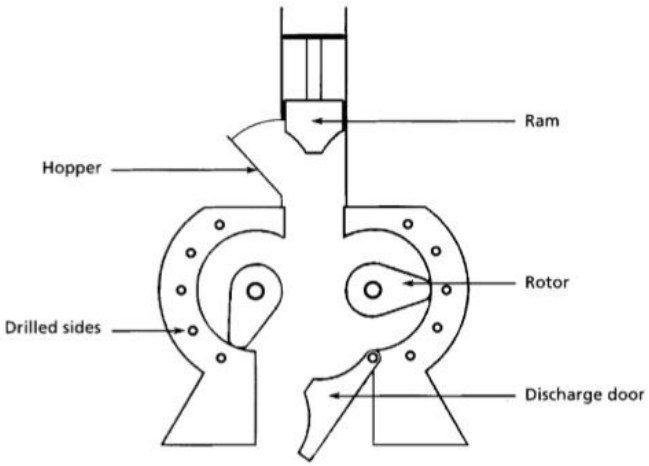


Figure 2.22: Conceptual cross-sections through an internal mixing machine, with tangential rotors [3].

2.4.3 Extruders

Extruders are conceptually a pump, consisting of a screw to move the material forwards, a barrel around the screw to contain the material, help it move, and provide

part of the temperature control. The back end has a hopper, sometimes with feed rollers, to put rubber into the screw, and the front end has a ‘head’ to hold a die, through which the rubber extrudes [3]. Conceptual view of basic extruder is shown at Figure 2.23.

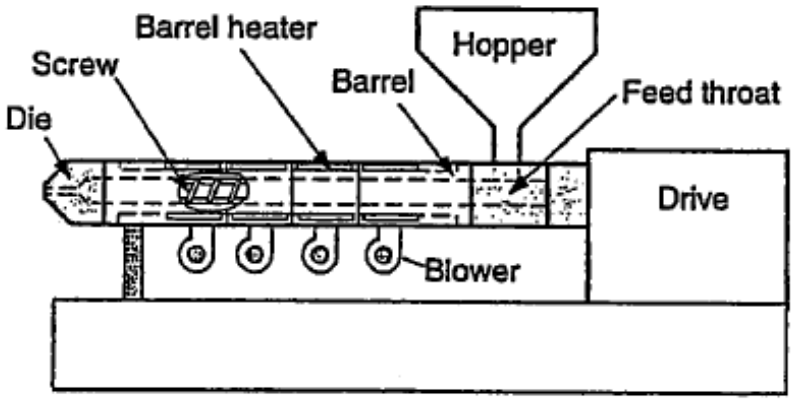


Figure 2.23 : Conceptual view of basic extruder [34].

Extruders that use pre-warmed rubber compound, hot feed extruders, (pre-warming on a mill for example) use a small ratio, for example 6:1, while those using rubber compound at room temperature, cold feed extruders, need a larger ratio, for example 12:l. This longer length is needed since the initial part of the screw is used to heat up the compound. Some extruders have a vent from the screw cavity through the barrel to the outside, to allow the escape of any air trapped in the compound.

The system is designed to build up compression at the discharge end, to ensure consolidation of the material in the head. This can be realized in a number of ways, such as reducing the screw pitch towards the front. An important design variable is the ratio of the length to the diameter of the screw, the L/D ratio.

Extruders are used to make hose and general profiles such as window channels, coated wires, and preforms for further processing. They can also be used to produce sheet rubber, where a large extruder makes a tube, which is immediately slit, producing a continuous sheet. [3]. Products produced include sheets, profiles, pipes, tubes, rods, wire/cable coverings and others [34].

2.5 Nanocomposites

Nanocomposites are a combination of two or more phases containing different compositions or structures, where at least one of the phases is in the nanoscale

regime. These materials exhibit behavior different from conventional composite materials with microscale structure, due to the small size of the structural unit and the high surface-to-volume ratio [35].

The three major advantages that nanocomposites have over conventional composites are as follows:

- Lighter weight due to low filler loading,
- Low cost due to fewer amounts of filler use and
- Improved properties (includes mechanical, thermal, optical, electrical, barrier, etc.) compared with conventional composites at very low loading of filler [36].

Nanocomposites are classified into three main classes, depending on the shape of the nanofiller, i.e., the number of dimensions of the dispersed particles in the nanometer range.

(a) *Nanoparticulate composites* composed of embedded isodimensional particles with three dimensions in the order of nanometers, such as spherical silica nanoparticles, semiconductor nanoclusters

(b) *Nanofilamentary composites* composed of a matrix with embedded (generally aligned) nanoscale diameter filaments. In this type, two dimensions are in the nanometer scale and the third one is larger, forming an elongated structure such as, carbon nanotubes or cellulose whiskers which are extensively studied as reinforcing nanofillers yielding materials with exceptional properties

(c) *Nanolayered composites* composed of alternating layers or sheets in which only one dimension is in the nanometer range. In this case, the filler is in the form of sheets (i.e., silicates) one to a few nanometers thick and hundreds to thousands nanometers long. Polymer-layered crystal nanocomposites belong to this group. These materials are almost exclusively obtained by the intercalation of the polymer (or a monomer subsequently polymerized) inside the galleries of layered host crystals. Nanolayered composites based on layered silicates have been more widely investigated; probably because of the abundance of the starting clay materials and the variety of advantages they offer [35].

Classification of clays as a function of the electrical charge is summarized at Table 2.7.

Table 2.7 : Classification of clays as a function of the charge of the layer [37].

Type of layers	Type of clays	Main features
Neutral layers	Pyrophyllite, talc, kaolinite	Layers joined together by van der Waals interactions and/or hydrogen bonds
Negatively charged clays	Phyllosilicates: e.g bentonites (Main component: montmorillonite)	The negative layer charge is exactly compensated by comoensating cations are located in the interlayer space
Positively charged layers	Hydrotalcite (HT), layered double hydroxides (HT-like family)	The positive layer charge is exactly compensated by comoensating cations are located in the interlayer space

2.5.1 Halloysite nanotubes (HNTs)

HNTs are a kind of natural clay from earth with hollow tubular structure and alumina-silicate groups on their surface. With large L/D ratio (dimensions of up to 10 μm in length, the inner diameter in order of 10-30 nm, and the outer diameter in order of 30-100 nm), HNTs provide improved properties for polymers, especially mechanical properties (tensile strength, modulus and dimensional stability), lower gas permeability, thermal stability, and flame retardancy. The chemical formula of HNTs is $Al_2[Si_2O_5(OH)_4].2H_2O$ [4-16]. It is similar with kaolinite structure; however HNTs differ from kaolinite with intermolecular water [12]. The tubular structure of HNTs is like multi- walled carbon nanotubes (MWCNTs), but HNTs are cheaper than MWCNTs [12]. Therewithal, due to the polar groups on their surfaces, HNTs can be well dispersed in the polymer matrices with compared to MWCNT [6]. Schematic notation of HNTs is shown in Figure 2.24.

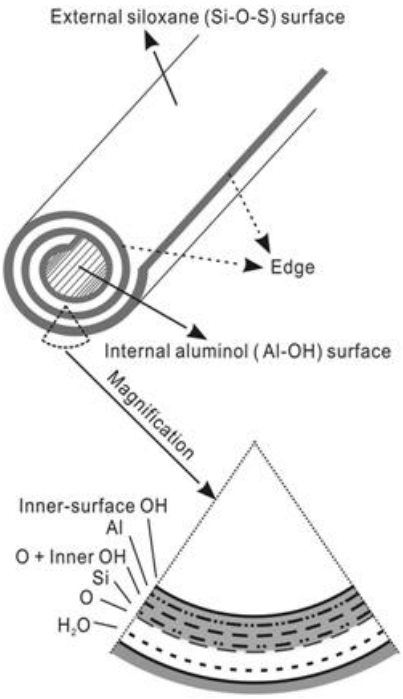


Figure 2.24 : Schematic notation of HNTs [38].

2.5.1.1 Modification of HNTs

Due to relatively lower compatibility of HNTs with rubber macromolecules, it is difficult to have homogeneous rubber/HNTs blends and this difficulty overtakes the positive contributions of HNTs in the compounds and makes it imperceptible [11]. For this reason, HNTs should be modified in order to increase hydrophobicity to permit it to interact with the rubber [4]. In literature, there are some attempts about surface modification of HNTs. Researches which done with γ-aminopropyltriethoxysilane modified HNTs, aminosilan modified HNTs or alkali activated HNTs can be found from literature [38,39,40]. Positive effects of reactive acids have been attributed to their capability on hydrogen bond formation between acid end groups and unsaturated rubber macromolecules [15,16]. IA is also considered as a modifier with its higher reactivity owing to double carboxylic groups at this study.

- **Itaconic acid (IA)**

IA is an odorless, white crystalline material which has another name as methylene succinic acid. It is solid form at room temperature and soluble in water, ethanol or aceton. IA is obtained from fermentation of funguses or carbohydrates. It is an

important agent for polymerization because of its reactive properties. It contains easily abstractable hydrogen atoms and a double bond [41,42]. The chemical structure of IA can be seen in Figure 2.25.

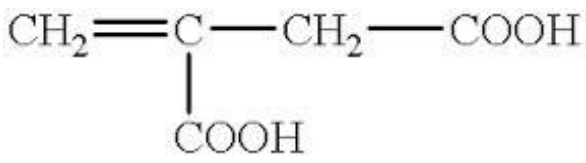


Figure 2.25 : Chemical structure of IA.

2.6 Literature Review

In this section, using of unmodified or modified HNTs as filler in the rubber matrix will be mentioned in the last decay.

Ismail et. al. examined thermal, physical, tensile, and morphological characteristics of (EPDM)/HNTs nanocomposites. Nanocomposites were prepared with different loading of HNTs between 0-100 phr. They observed that, HNTs could be well dispersed in EPDM matrix. On the other hand, there were also interfacial and inter-tubular interactions between HNTs and EPDM, and edge-to-edge and face-to-edge interactions between HNTs, especially at high HNTs loading. By virtue of this, tensile strength, stiffness, and ductility of EPDM/HNTs nanocomposites improved [43]. In their next study, Ismail and co-workers investigated the effect of HNTs on NBR. The resulting nanocomposites were characterized by different techniques, such as thermogravimetric analysis (TGA) and SEM. Curing time of rubber decreased by incorporation of HNTs; tensile strength, tensile modulus, elongation at break, and thermal stability of the NBR/HNTs nanocomposites exhibited an increase up to the optimum HNTs loading. Owing to good interaction between HNTs and NBR, the stiffness and ductility of nanocomposites presented enhanced properties [6]. At another study Ismail and co-workers used different mixing methods (mechanical and solution mixing) for preparation of NR/HNTs nanocomposites. They observed that scorch time, cure time and maximum torque values of nanocomposites increased by addition of HNTs for both mixing methods. But longer scorch and cure time of nanocomposites prepared by solution mixing method than nanocomposites prepared via mechanical mixing method are obtained. Nanocomposites prepared by solution

mixing method showed higher tensile strength, tensile modulus, fatigue life and decomposition temperature at lower percentage of weight loss than mechanical mixing method. SEM images showed better dispersion of HNTs in nanocomposites prepared via solution mixing method than mechanical mixing method [12].

Rooj and co-workers studied on fluoroelastomers (FKM) which were reinforced by HNTs. They observed that HNTs amount affects the mechanical and dynamic mechanical properties. Encouraging results were obtained from transmission electron microscopy (TEM) images. HNTs could be dispersed in FKM matrix up to 10 phr, homogenously. Dynamic mechanic analysis results showed that there was an efficient interaction between FKM matrix and HNTs. The other effect of HNTs on FKM/HNTs nanocomposites was improved thermal stability. A magnificent influence of thermal stability was observed at 5 phr [44].

Guo et al were used methacrylic acid (MAA) to improve the performance of SBR/HNTs nanocomposites by direct bending. The interactions between HNTs and MAA or in situ formed zinc methacrylate (ZDMA) were characterized fully. The significantly improved mechanical properties, vulcanization behavior and morphology were correlated to the largely improved interfacial bonding between HNTs and rubber and significantly enhanced dispersion of HNTs [15]. Their another study is SBR/HNTs nanocomposites modified by sorbic acid (SA). They used SA to improve the performance of SBR/HNTs nanocomposites by direct bending. The strong interfacial bonding between HNTs and rubber matrix is resulted through SA intermediated linkages. SA bonds SBR and HNTs through grafting copolymerization/hydrogen bonding mechanism. Significantly improved dispersion of HNTs in virtue of the interactions between HNTs and SA was achieved. Promising mechanical properties of SA modified SBR/HNTs nanocomposites were obtained. The changes in vulcanization behavior, mechanical properties and morphology were correlated with interactions between HNTs and SA the largely improved dispersion of HNTs [16].

Jia et. al. were studied with SBR/modified HNTs (SBR/m-HNTs) nanocomposites. Complex of resorcinol and hexamethylenetetramine (RH) was used as the interfacial modifier because of dispersity problems of HNTs. The structure, morphology and mechanical properties of SBR/m-HNT nanocomposites, especially the interfacial

interactions, were investigated. SEM and TEM observations showed that RH can not only facilitate the dispersion and orientation of HNTs in SBR matrix at nanometer scale, but also enhance the interfacial combination between HNTs and rubber matrix. Fourier transmission infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS) investigations confirmed that a number of hydrogen bonds were formed between the phenol hydroxyl groups in resorcinol-formaldehyde resin derived from RH and the oxygen atoms in Si—O bonds or hydroxyl groups on HNTs surfaces. The m-HNTs modified with RH have significant reinforcing effect on SBR vulcanizates. They observed that RH as a good interfacial modifier can remarkably improve mechanical properties of SBR/HNT composites. The substantial improvement of comprehensive properties for SBR/m-HNT nanocomposites can be attributed to good dispersion and orientation of HNTs in SBR matrix at nanometer scale and the enhanced interfacial interaction between HNTs and rubber matrix [11].

Pasbakhsh and co-workers examined the EPDM/modified HNTs nanocomposites. HNTs were modified by γ-methacryloxypropyltrimethoxysilane (MPS) to improve their dispersion in EPDM. The tensile strength and tensile modulus at 100% elongation of the nanocomposites were higher than those of EPDM/unmodified HNTs nanocomposites while the elongation at break slightly decreased after modification of the HNTs. SEM and TEM studies clarified the better dispersion of the modified HNTs in the EPDM matrix. FTIR and TGA indicated that γ-MPS had partially penetrated into the HNTs and interacted with Si-O groups on the surfaces of the HNTs [45].

Rybinski and co-workers presented the results of the effect HNTs activated with sodium hydroxide on thermal properties and combustibility of SBR. The results of these investigations have been compared with influence of montmorillonite modified by means of various organic compounds on the same properties of styrene–butadiene rubber. They concluded that the nanofillers used do not explicitly influence the thermal stability of the nanocomposites tested but they decrease the thermal decomposition rate of these materials under thermo-oxidative conditions. Both HNTs and modified montmorillonite (nanofiller) decrease the flammability of the cross-linked SBR, which is also accompanied by a reduction in fire hazard resulting from the use of the nanocomposites tested [4].

In the literature, there are only a few attempts on using CB and HNTs together as dual fillers. Salleh and co workers used NR with HNTs/CB hybrid filler at various filler loading. The curing characteristics, fatigue life and morphological properties of NR/HNTs/CB nanocomposites were studied. Nanocomposites which include HNTs exhibited longer scorch and curing times. In addition to this, fatigue resistance of compounds was improved by HNTs incorporation. This can also be seen from SEM images of tear fractured surfaces [46].

Ismail and co-workers studied the effects of CB replacement with HNTs in NR based compounds. Total hybrid fillers were kept constant at 40 parts per hundred rubbers (phr) and were prepared using laboratory two-roll mill. Compounds exhibited longer curing and scorch times, lower tensile properties and an increment in swelling percentage with increasing amount of HNTs. However, fatigue tests and elongation at break data were satisfactory. HNTs can be dispersed homogenously in rubber matrix for lower loading ratios [14]. At their study, Ismail and co-workers examined curing characteristics, tensile properties, rubber-filler interaction and morphological characteristics of NBR composites with HNTs and silica or CB. The tensile strength and modulus of both composites decreased, whereas elongation at break and maximum torque increased with increasing the silica or carbon black content. However, both composites show opposite trends for cure time and scorch time, where NBR/HNTs/Silica composite exhibited an increasing trend, while NBR/HNTs/CB composite shows the decreasing trend. The rubber-filler interaction studies showed that CB is a more capable reinforcing filler than silica [47].

Polikelispaa and co-workers have also a study on the properties of plasma-modified HNTs and CB filed NR/BR blends. The existing of HNTs in filler system was found to be quite efficient on curing properties. Dynamic test results showed that, addition of HNTs caused higher values in energy dissipation. This means HNTs filled compounds had better wed skid resistance but higher rolling resistance [48].

3. EXPERIMENTAL

3.1 Materials

3.1.1 Styrene-butadiene rubber (SBR)

SBR 1502 (Voronezh, styrene content is 23%) was used as rubber matrix. It was kindly obtained from Arsan Rubber Company, Turkey.

3.1.2 Halloysite nanotube (HNTs)

HNTs was kindly obtained from Eczacıbaşı Esan, Turkey. The chemical analysis of HNTs were made and the results found as; 43.3% SiO_2, 38.4% Al_2O_3, 0.7% Fe_2O_3, 0.1 TiO_2, 0.08 CaO, 0.12 MgO, 0.27 Na_2O and 0.12 K_20. It was used as flame retardant filler for SBR.

3.1.3 Itaconic acid (IA)

Systematic name of IA is 2-methylene succinic acid. It is a product of Alfa Aesar Chemical Company with 99% purification. It was used without any purification procedure for modification agent for HNTs (m.p. = 165- 167^oC).

3.1.4 Aromatic oil

Aromatic oil was kindly procured from Arsan Rubber Company, Turkey. Its viscosity at 100^oC, 65-82 Sayboult universal second (SSU) and its flash point is minimum 210 ^oC. It was used as plasticizer in SBR compounds.

3.1.5 Carbon black (CB)

CB was obtained from RPM Prod, Turkey. It was used as secondary filler for SBR. It belongs to N330 ASTM group. Particle size and surface area of CB is 26-30 nm and 70-99 m^2/g, respectively.

3.1.6 N-isopropyl-N'-phenyl-p-phenylene-diamine (IPPD)

IPPD was obtained from RPM Prod., Turkey. It was used as antioxidant in compounds. Moleculer formula of IPPD is $C_{15}H_{18}N_2$.

3.1.7 2,2,4-trimethyl-1,2-dihydroquinoline (TMQ)

TMQ was obtained from RPM Prod., Turkey. It was used as antioxidant in compounds. Moleculer formula of TMQ is $C_{12}H_{17}N$.

3.1.8 Zinc oxide (ZnO)

ZnO was obtained from RPM Prod., Turkey. It was used as activator with stearic acid for sulfur.

3.1.9 Stearic acid

Stearic acid was obtained from RPM Prod., Turkey. It was used as activator ZnO for sulfur. Moleculer formula of stearic acid is $CH_3(CH_2)_{16}CO_2H$.

3.1.10 Tetramethyl thiuram disulfid (TMTD)

TMTD was obtained from RPM Prod., Turkey. It was used as accelerator for sulfur.

3.1.11 Sulfur

Sulfur was obtained from RPM Prod., Turkey. It was used as curing agent for compounds.

3.2 Equipments

3.2.1 Equipments used for compounding

3.2.1.1 Two roll mill

Laboratory type 150 mm two roll mill was used to prepare nanocomposites. It has friction factor of 1:1.1. Figure 3.1 shows an example of laboratory type two roll mill.

Figure 3.1 : Laboratory type two roll mill.

3.2.2 Equipments for unvulcanized compound

3.2.2.1 Differential scanning calorimeter (DSC)

Glass transition temperatures (T_g) and curing peak temperatures of the compounds were obtained using a differential scanning calorimeter (DSC, Mettler Toledo DSC1).

3.2.2.2 Density measuring instrument

The density of compounds was measured by Mettler Toledo XS204 Delta Range Analytical Balance.

3.2.2.3 Moving die rheometer (MDR)

Cure characteristics of uncured compounds were determined with a moving die rheometer (MDR, MonTech MDR 3000 Basic) at 180 °C according to ASTM D2084, after conditioning for least 24 hours at ambient conditions. The used MDR is shown at Figure 3.2.

Figure 3.2 : Moving die rheometer (MDR).

Rheometer, measures the flow behaviour rubber compounds during vulcanization and gives the rheometer curve. It applies to rubber compound an oscillation at desired temperature and pressure. As a result of the increasing of crosslinking density, torque force increases which are effective on the rotation center of equipment. MDR gives this increment as a function of time which can be seen from Figure 3.3.

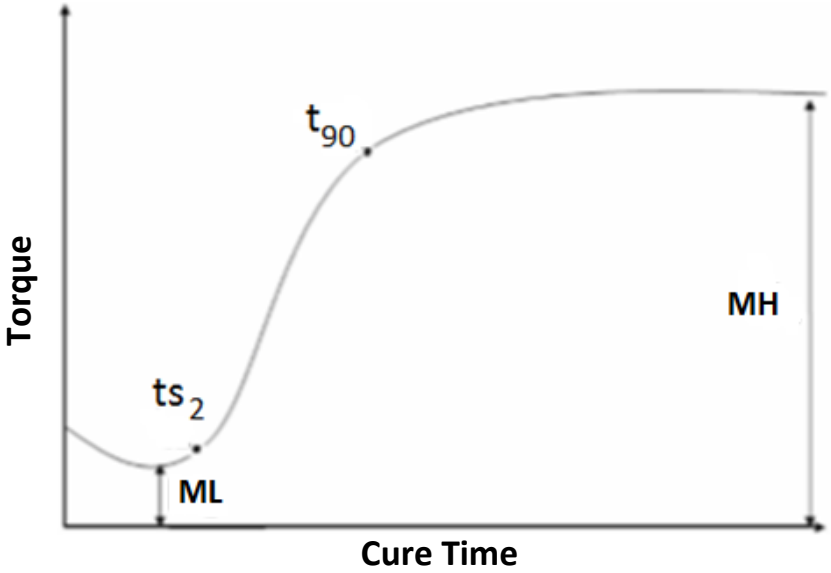


Figure 3.3 : Typical rheometer curve [17].

In a crosslinking isotherm for elastic response ML is the minimum torque value and gives the minimum viscosity of rubber compound. MH, is the final rheometer indication constant in time, on completion of crosslinking reaction and give the maximum torque of compound. MH, if a constant value for ML, is assumed then MH gives information about the curative system, and therefore the degree of cross-linking of the elastomer. If insufficient curatives are mixed into the batch, then MH will be low. ts_2 (scorch time) is the time after two torque units above ML is reached in an elastic torque curve. Scorch time is essential to the safe processing of a rubber compound, on any rubber machinery that further shapes the compound while heating it up. t_{90} is the time required for elastic torque curve to reach 90% of maximum torque time. M_t is the rheometer torque value at any specified time (t).

From the crosslinking isotherms of an MDR instrument, one can also observed t10, t50, S''@ML, S''@MH, tan δ@ML, tan δ@MH, i.e., time required for elastic torque curve to reach 10% and 50% of maximum torque, respectively, minimum viscous value reading, maximum viscous torque reading, ratio of minimum viscous torque and minimum elastic torque, and ratio of maximum viscous torque and maximum elastic torque, respectively [3,17].

3.2.2.4 Hot press

Curing and molding were performed on a hydraulic press for their own optimum cure times, at 180 ^{o}C and under 150 bar pressure. The conceptual view of hydraulic hot press can be seen from Figure 3.4. Samples were handled as casts with 2 mm thickness for after-vulcanization measurements.

The uncured pieces of compound placed in the mold are known variously as preforms, billets or load weights. Normally the weight of this preform will be chosen to be a few percent (from two to ten percent) above the weight of the final product, to ensure a fully formed product and to give an extra 'push' for expulsion of any residual trapped air. The preform is placed in the bottom cavity and the top mold section placed on it by hand. If a significant number of moldings are to be made, it is often advantageous to fix the two halves of the mold to their respective press platens [3].

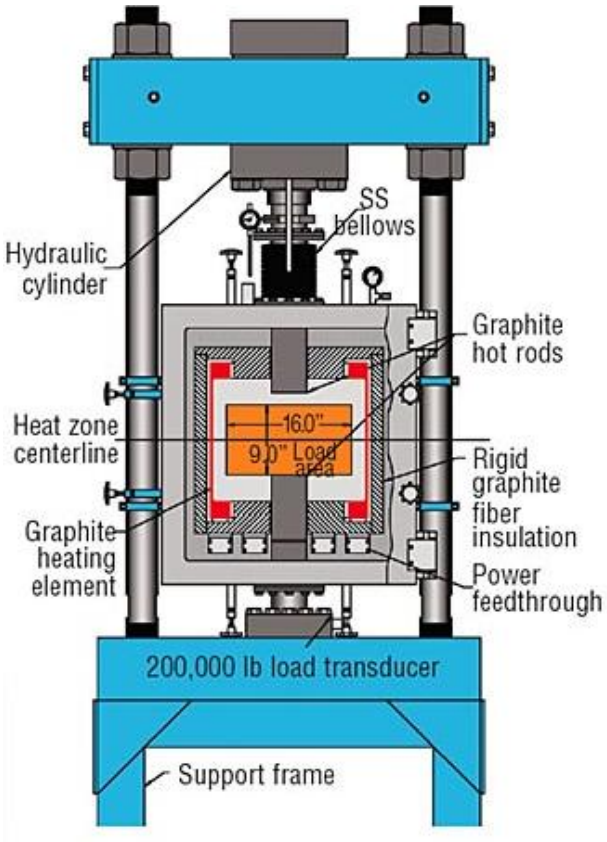


Figure 3.4 : Hydraulic hot press.

3.2.3 Equipments for vulcanized compounds

3.2.3.1 Tensile test machine

Tensile properties of the vulcanizates were determined by using Zwick 0.5 Universal Tensile Testing Machine, according to ASTM D412. The machine was equipped with an extensometer and had Zwick 8195 type, 1kN pneumatic grips. The load cell was capable of applying 500 N force and testing samples up to 500 mm / min speed.

3.2.3.1 Hardness measurement instrument

Hardness values were measured by using a Shore A type durometer according to ASTM D2240. After 20 seconds of the beginning of the test, measured values were recorded. For every sample, at least 3 parallel measurements were done. Averages of the values were calculated and recorded.

3.2.8 Scanning electron microscopy (SEM)

A scanning electron microscope (SEM) (JEOL/JSM-6060) was employed to examine the morphology of the surfaces of the tensile fractured nanocomposites. The samples were prepared by applying, gold coatings.

3.2.9 Limiting oxygen index (LOI) instrument

2012 manufacturing MARES LOI machine was M-LOI model. It was used for determining a numerical measure of flammability.

3.3 Methods

3.3.1 Preparation of compounds

The compounds of nanocomposites were prepared by using laboratory type two roll mill. SBR, antioxidants (TMQ and IPPD), IA, fillers (HNTs and CB), aromatic oil, stearic acid, zinc oxide, TMTD and sulpur were put to mill respectively. Labeling methodology of compounds can be seen from Figure 3.5 and 3.6. The recipes of compounds are listed in Table 3.1 and 3.2. It is shown that mill processing time for every material at Table 3.3.

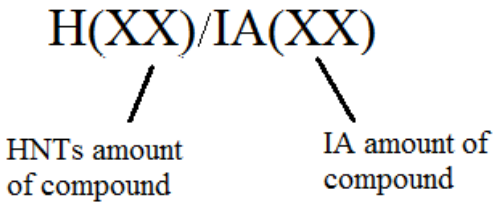


Figure 3.5 Labeling methodology for compounds without CB.

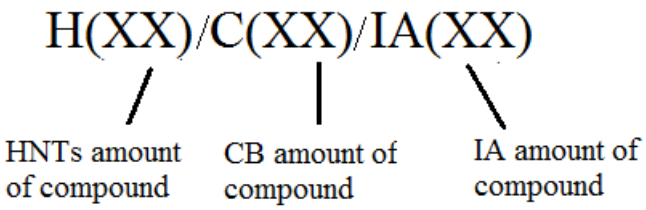


Figure 3.6 Labeling methodology for compounds with CB.

Table 3.1 : Compound recipes (without CB).

	H0/IA0	H0/IA5	H20/IA0	H20/IA0.5	H20/IA1	H20/IA2	H20/IA5	H30/IA0	H30/IA5
Materials	**Components (phr)**								
SBR	100	100	100	100	100	100	100	100	100
CB	-	-	-	-	-	-	-	-	-
HNTs	-	-	20	20	20	20	20	30	30
IA	-	5	0	0.5	1	2	5	0	5
Oil	-	-	5	5	5	5	5	5	5
IPPD	1	1	1	1	1	1	1	1	1
TMQ	1	1	1	1	1	1	1	1	1
ZnO	5	5	5	5	5	5	5	5	5
St.Ac.	2	2	2	2	2	2	2	2	2
TMTD	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Sulfur	1	1	1	1	1	1	1	1	1

Table 3.2 Compound recipes (with CB).

	H0/C40/IA0	H0/C40/IA0.5	H0/C40/IA1	H10/C30/IA0.5	H10/C30/IA1	H20/C20/IA1
Materials	**Components (phr)**					
SBR	100	100	100	100	100	100
CB	40	40	40	30	30	20
HNTs	-	-	0	10	10	20
IA	-	0.5	1	0.5	1	1
Oil	5	5	5	5	5	5
IPPD	1	1	1	1	1	1
TMQ	1	1	1	1	1	1
ZnO	5	5	5	5	5	5
St.Ac.	2	2	2	2	2	2
TMTD	1.5	1.5	1.5	1.5	1.5	1.5
Sulfur	1	1	1	1	1	1

SBR: Styrene butadiene rubber; CB: Carbon black N330; HNTs: Halloysite nanotubes; IA: Itaconic acid; Oil: Aromatic oil; IPPD: N-Isopropyl-N'-phenyl-p-phenylene-diamine; TMQ: 2,2,4-trimethyl-1,2-dihydroquinoline; St. Ac: Stearic Acid TMTD: Tetramethyl thiuram disulfid.

Table 3.3 : The steps of rubber compounding.

Process	Time (min)
Mastication of rubber	7
Adding oil and filler	10
Adding ZnO	5
Adding TMQ and IPPD	5
Adding TMTD	5
Adding Sulfur	5
Last Mixing	5
Total	42

3.3.2. Characterization of compounds

3.3.2.1 Curing characteristics

Glass transition temperatures and curing peak temperatures of compounds were determined by DSC equipment for -80-250 °C temperature range and 10 °C/min heating rate. DSC results can be seen at section 4.1. Curing times and curing characteristics (ML, MH, ts_2 and t_{90}) of the compounds were obtained by using MDR at 180^{o}C according to ASTM D2084. Measurements were done for least three samples and average values were calculated. Density measurements were done to determine the mass of compounds which will be moulded at hydraulic hot press. Firstly the specimen was weighted in air and then the same specimen was weighted in water. Density of water was assumed to be 1 g/cm^3. So density of specimen was found with mass in air per mass in water. Measurements done for three samples and average values were calculated.

3.3.3 Preparation of nanocomposites

Curing and molding were performed on a hydraulic press for their own optimum cure times which obtained at MDR. The curing times were different for compounds depending on their HNTs, IA or CB contents and they were between 2.5-10 minutes.

The press temperature was 180^{o}C and pressure was 150 bar. Used mould for vulcanization is shown at Figure 3.7. 2 mm sheet shaped vulcanizates were taken from the moulds and test samples were prepared in required dimensions from the sheets with using sharp knives which shown at Figure 3.8.

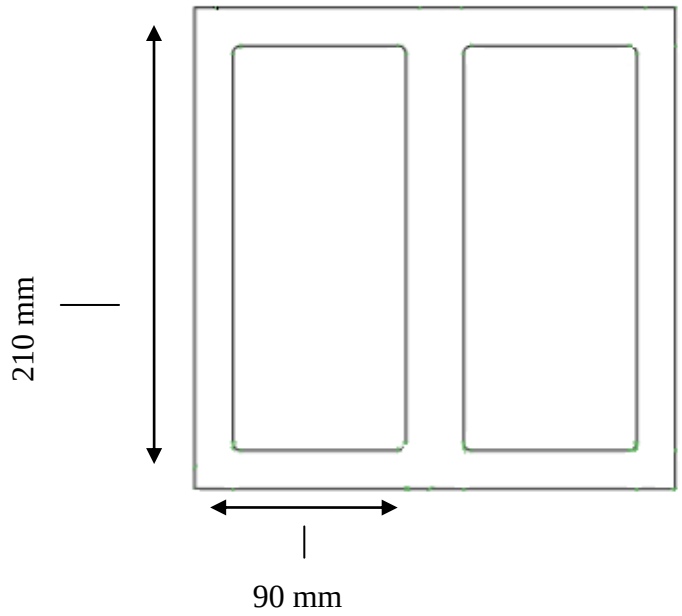


Figure 3.7 : Shape and dimensions of 2 mm thick mould.

3.3.4 Characterization of nanocomposites

3.3.4.1 Tensile test

2 mm sheet shaped vulcanizates were taken from the moulds and test samples were prepared in required dimensions from the sheets with using sharp knives. At least, 5 specimens were used for measurement. The tensile tests were carried out at 500mm/min rate and tensile strength, elongation at break, young modulus values were obtained. The error margins calculated as ±0.15 MPa, 54.4% and 0.12 MPa, respectively. Figure 3.5 shows that tensile test sample for ASTM D412 standart.

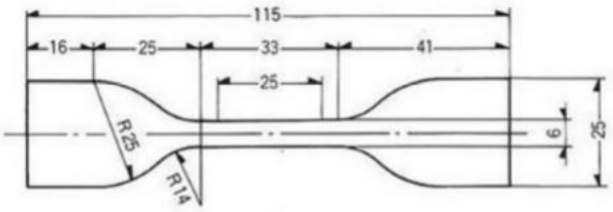


Figure 3.8 : Tensile test sample for ASTM D412.

3.3.4.2. Crosslinking densities

Crosslinking densities of nanocomposites (CLDs) were determined with Young's modulus (E) approach which is obtained from tensile tests. This method is easy and useful because it is really complicated to define crosslinking density from swelling measurements. Sekkar and co-workers studied on experimental approaches of the crosslink density of urethane networks based on hydroxyl-terminated polybutadiene [49]. E is related with CLD as in Equation (3).

$$E = 3\upsilon RT \quad \textbf{(3.1)}$$

where υ is CLD, R is universal gas constant (8.314 J mol^{-1} K^{-1}), T is absolute temperature (K).

3.3.4.3 Shore A hardness test

According to standard measurement (ASTM D 2240); the hardness measurement were done. Hardness test specimens had 6 mm thickness and at least three parallel measurements were done. Their average values were recorded.

3.3.4.4 Morphological properties

Morphology of the tensile fractured surfaces of the vulcanizates was observed using SEM. Prior to SEM observation, the fractured surface sample was sputter coated with gold.

3.3.4.5 Limiting oxygen index (LOI) measurements

A limiting oxygen index instrument, which was described at Section 3.2.9, was used to determine the flammability properties of H20/IA0 and H20/IA1 nanocomposites. The samples for LOI measurements had different dimensions because of special test dimensions requirement for this test. A different mould was used to prepare LOI samples. The dimensions of samples were 5cmx10cmx0.6 cm.

4. RESULTS AND DISCUSSION

In this study, effects of IA have been evaluated as a modifier between HNTs and SBR matrices in SBR/HNTs and SBR/HNTs/CB compounds and nanocomposites. Compounds were prepared at laboratory type two roll mill with and without CB. Total number of compounds were 15 (9 of them without CB, remain with CB). The T_g values and curing peak temperatures ($T_{p)}$ of the compounds were determined by DSC. DSC results were discussed at section 4.1. To obtain curing characteristics and curing time of the compounds, measurements were done at a MDR. The curing times and characteristics of compounds can be found at Section 4.2. Density measurements were done to obtain weight of compounds which were moulded and cured at hydraulic hot press. The density values were between 0.76-0.96 g/cm^3. The compounds were cured at hydraulic press at 180 ^oC during determined time at rheometer. Mechanical properties of nanocomposites (tensile strength, elongation at break, Young's modulus) were obtained with a tensile test machine and crosslinking densities were procured with Young's modulus values. Depending on content of nanocomposites, mechanical properties showed some discrepancies. Hardness values of nanocomposites were measured by using a Shore A type durometer. The results were given and discussed at Section 4.3. Morphological properties of the nanocomposites were obtained with a SEM. The taken micrographs and discussions can be found at Section 4.4.

Compounds which include excess IA (H0/IA5, H20/IA5 and H30/IA5) could not be cured because of their insufficient curing times as will be mentioned at section 4.2. So tensile test, hardness test, SEM measurement and LOI measurement did not been applied on these uncured compounds.

4.1 Thermal Properties of Compounds

T_g and T_p values of compounds were mentioned as thermal characteristics. These values were measured by DSC. Thermal properties have been discussed as in two groups which are without and with CB.

The T_g values of the compounds (SBR/HNTs) which are without CB did not change significantly by adding HNTs or IA as can be seen from Table 4.1 and Figure 4.1. So, the T_g values did not affect with filler or modifiying agent existence or amount. It is interested with rubber type. The rubber type is the same for all compounds. It explains the same T_g values. The T_p values of the without CB compounds are given in Table 4.1 and Figure 4.2. As seen, existence of HNTs increased T_p by 3-5 ^oC when H0/IA0-H20/IA0 and H0/IA0-H30/IA0 compared to each other. It can be said that, the existence of HNTs is not so effective on T_p values. Curing shifted to 30 ^oC higher temperatures than the other compounds by using 5 phr IA (H0/IA0 to H0/IA5; H20/IA0 to H20/IA5; H30/IA0 to H30/IA5). This evaluation represents that the existence of IA is quite effective on optimum T_p values of SBR based rubber compounds and causes a significant delay in curing reaction and 5 phr IA so much for these compounds. It is not feasible and convinient when compared the other compounds. The rheometer results support these findings, too. Beside this, T_p value of compounds increased by IA loading. For HNTs-IA incorporation, amount of IA is more effective on changing and increasing T_p when H0/IA0, H20/IA0 and H20/IA5 compounds compared each other.

Table 4.1 : T_g and T_p values of compounds without CB for 100 phr SBR.

	T_g (^oC)	T_p (^oC)
H0/IA0	-51.9	178.7
H0/IA5	-52.7	207.8
H20/IA0	-51.7	183.8
H20/IA0.5	-51.3	185.8
H20/IA1	-51.4	187.6
H20/IA2	-52.8	190.6
H20/IA5	-52.6	209.9
H30/IA0	-53.1	180.8
H30/IA5	-52.1	216.8

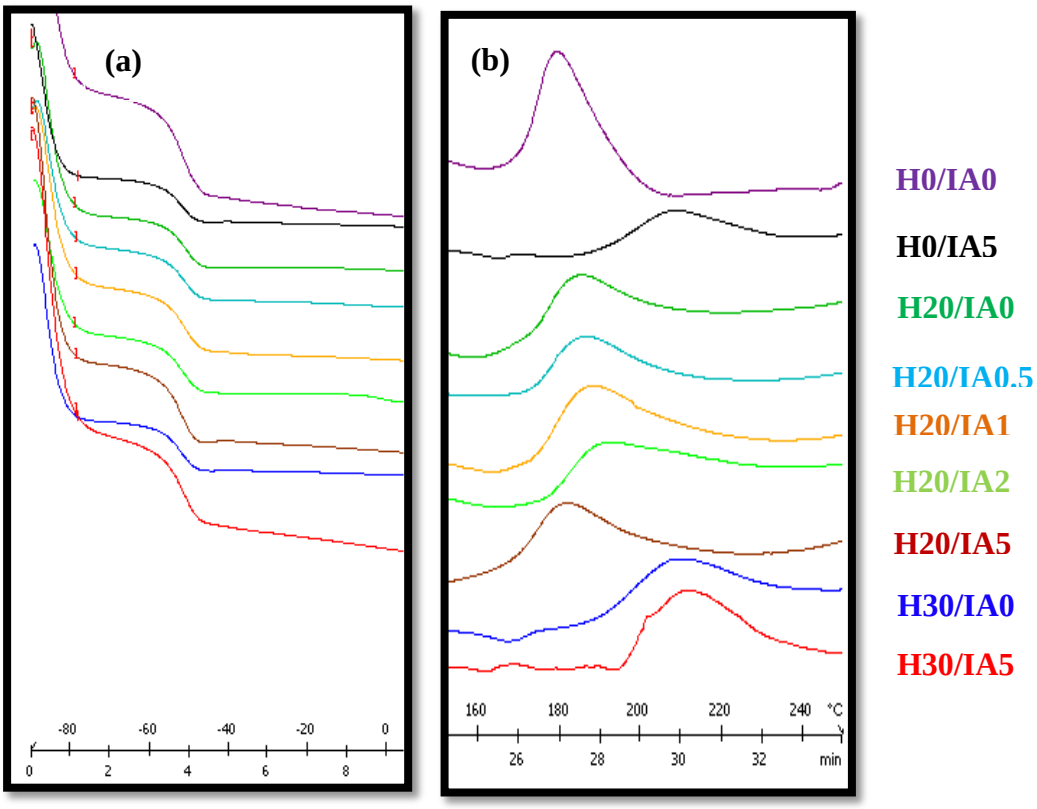


Figure 4.1 : DSC thermograms of compounds without CB for 100 phr SBR

(a) T_g, **(b)** T_p

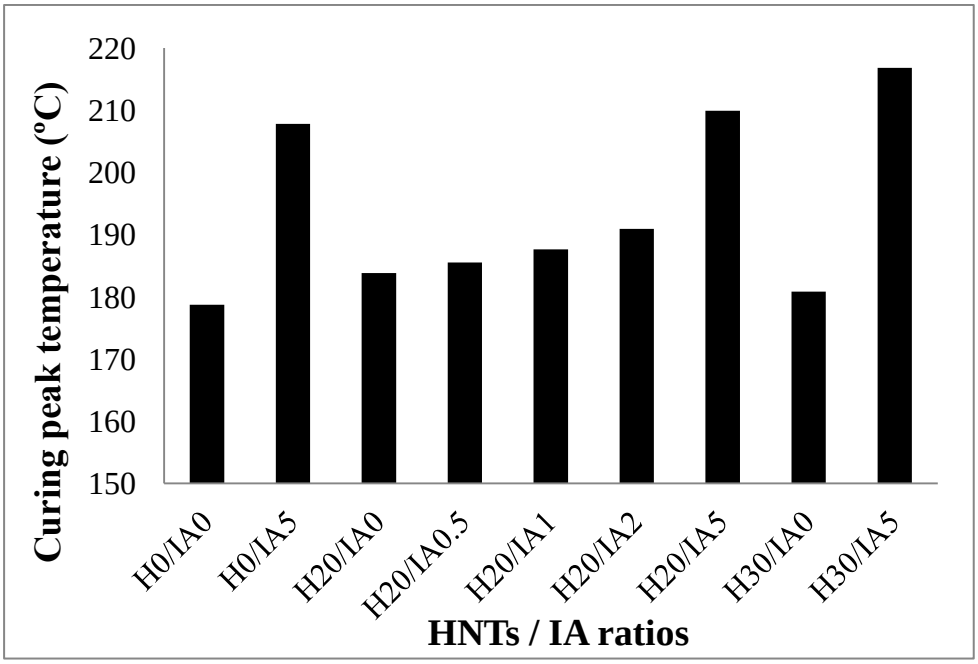


Figure 4.2 : T_p of the compounds without CB for 100 phr SBR.

In Table 4.2, T_g values and curing peak temperatures for CB containing compounds (SBR/HNTs/CB nanocomposites) were listed and DSC thermograms are shown in Figure 4.3. T_g values are very close to each other as can be seen from Table 4.2. Curing peak temperatures of compounds with CB, can be seen from Figure 4.4. Increasing of HNTs and also decreasing of CB amount caused a decrement when H0/C40/IA0.5 and H10/C30/IA0.5 compounds are compared. IA affects the curing peak temperature but this effect is not as significant as SBR/HNTs nanocomposites. In the case of H10/C30 compounds, increase in amount of IA even for 0.5 phr (0.5 to 1 phr) carries the curing peak temperature from 175.9 to 182.6 ^{o}C. In the light of these findings, it is concluded that, presence of HNTs makes curing delay action of IA more dominant and amount of IA should be optimized to have satisfactory curing temperatures and so curing rates in SBR/HNTs and SBR/HNTs/CB nanocomposites.

Table 4.2 : T_g and T_p values of compounds with CB for 100 phr SBR.

	Tg (ºC)	**T_p (ºC)**
H0/C40/IA0	-51.6	177.3
H0/C40/IA0.5	-52.5	179.7
H0/C40/IA1	-53.9	179.5
H10/C30/IA0.5	-53.1	175.9
H10/C30/IA1	-53.1	182.6
H20/C20/IA1	-54.9	182.1

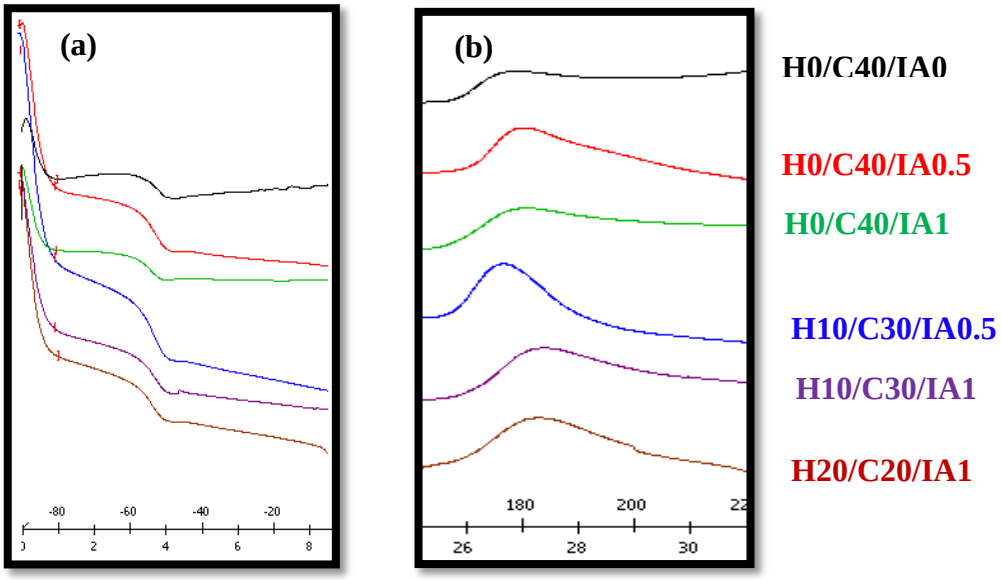


Figure 4.3 : DSC thermograms of compounds with CB for 100 phr SBR **(a)** T_g **(b)** T_p.

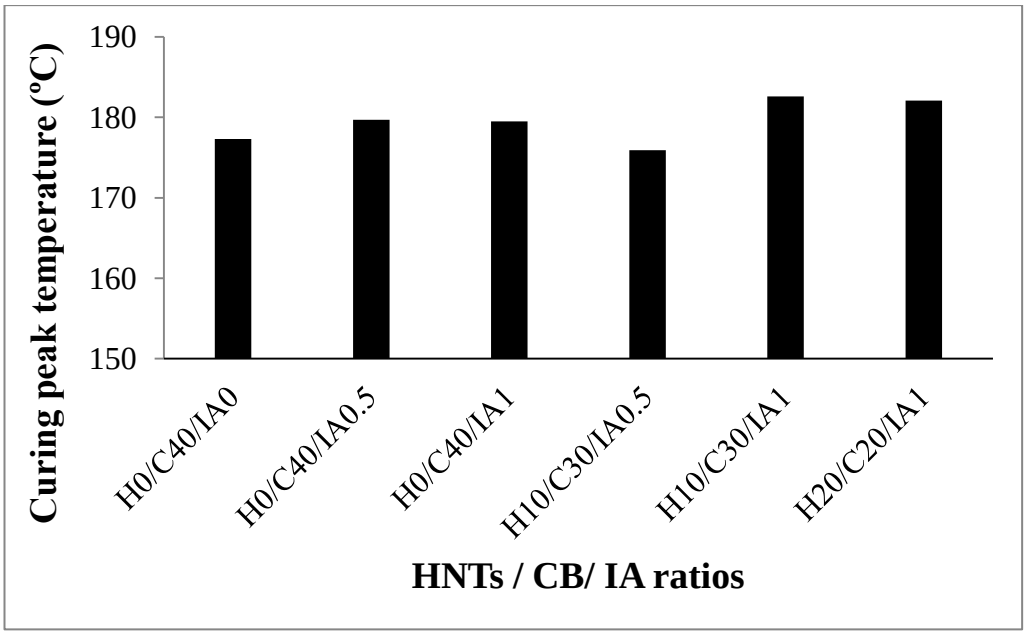


Figure 4.4 : T_p of the compounds with CB for 100 phr SBR.

4.2 Cure Characteristics of Compounds

Rheometer measurement is a necessary method for rubber compounds. It suggests about vulcanization chareacterists of compounds.

Important parameters (ML, MH, ts_2, t_{90}) of SBR/HNTs and SBR/HNTs/CB compounds were obtained by using a MDR at 180°C. Rheometer curves and numerical values of these parameters of SBR/HNTs and SBR/HNTs/CB compounds are given in Tables 4.3, 4.4 and Figures 4.5, 4.6, respectively. Cure extent and cure rate index (CRI) were calculated by using Equations (1) and (2) [50].

$$Cure\ extent\ (dNm) = M_H - M_L \quad \textbf{(4.1)}$$

$$CRI = \frac{100}{t_{90} - ts_2} \quad \textbf{(4.2)}$$

MH, if a constant value for ML, is assumed that MH gives information about the curative system, and therefore the degree of crosslinking of the elastomer [3] As can be seen from Table 4.3 an 4.4, ML values are close to each other or same. So, cure extent values can give suggestions about degree of crosslinking of the compounds. On the other hand, CRI is related with the cure rate of compounds [50,51].

As can be seen from Table 4.3, ML values of all compounds can be assumed as unchanged while MH, which can be represented as an indicator for mechanical

properties of the compounds after vulcanization, decrease significantly by loading HNTs and also IA. Maximum ML value belongs to H30/IA0. Optimum cure times of H0/IA5, H20/IA5 and H30/IA5 are nearly 30 minutes and 10 times higher than the other compounds. These cure times are not appropriate for feasible material production. This finding supports their high curing peak temperatures which determined on DSC. On the other hand, MH values are low for these compounds. Cure extent values are low and CRI are high for H0/IA5, H20/IA5 and H30/IA5. This is another evidence for low mechanical properties and curing challenges for these compounds. For this reason, these compounds were not considered in physical mechanical, morphological and flammability properties tests. HNTs incorporation causes a systematic decrease in optimum cure times of H0/IA0, H20/IA0, and H30/IA0 compounds. However, MH values of H20/IA0 and H30/IA0 lower than H0/IA0 compound. Cure extent of H30/IA0 is higher than H20/IA0. So the crosslinking amount of H30/IA0 is higher than H20/IA0. This situation explains higher MH value of H30/IA0 than H20/IA0. At the same time, H30/IA0 has lower cure rate then H20/IA0. IA effects optimum cure time by a slight increase, especially after 1 phr loading. On the other hand, when H20/IA0.5, H20/IA1 and H20/IA2 compounds are considered, their MH values decrease with compared to H20/I0. So IA is responsible on MH value decrement for these compounds. Their cure extent values are lower than H20/IA0, as expected.

Table 4.3 : Rheological properties of compounds (without CB for 100 phr SBR).

	H0/IA0	**H0/IA5**	**H20/IA0**	**H20/IA0.5**	**H20/IA1**	**H20/IA2**	**H20/IA5**	**H30/IA0**	**H30/IA5**
ML (dNm)	0.7	0.6	0.7	0.7	0.7	0.7	0.7	0.9	0.8
MH (dNm)	6.6	3.0	4.6	4.3	4.0	3.2	3.2	5.0	3.8
t_{s2} (min)	1.2	21.8	1.2	1.3	1.5	2.7	20.6	1.1	12.4
t_{90}(min)	2.7	30.3	2.1	2.1	2.2	3.8	34.2	1.8	29.4
Cure extent	5.8	2.4	3.8	3.6	3.3	2.5	2.5	4.1	3.0
CRI (min^{-1})	64.9	11.7	111	125	143	84	7.6	135	5.9

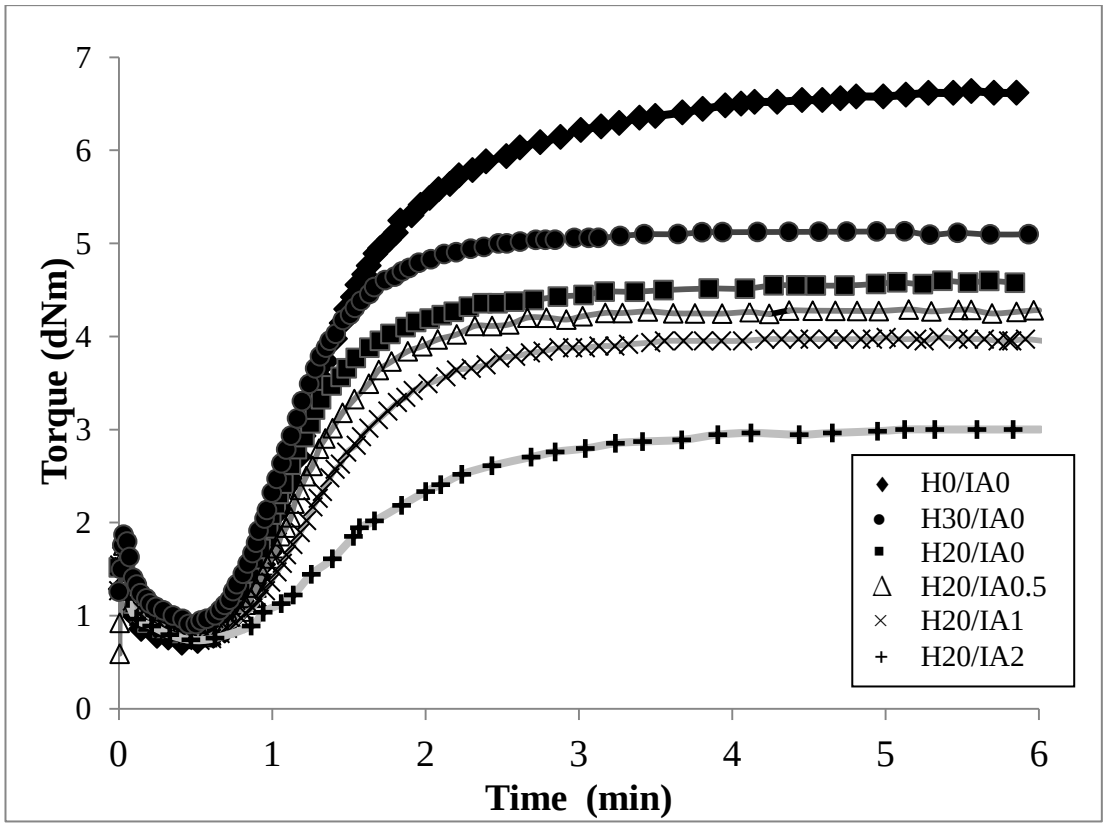


Figure 4.5 : Rheometer curves of the compounds at 180 ^{o}C (without CB for 100 phr SBR).

For the compounds with CB, ML values of all compounds can be assumed unchanged as compounds without CB. Their ts_2 and t_{90} values are almost the same but MH, cure extent and CRI values have some discrepancies. Existence of CB provided moderate optimum cure times and enhanced MH values which are depicted in Table 4.4 and Figure 4.6. As can be seen from Table 4.4, MH values are significantly lower for the compounds which contain HNTs and IA. Beside this, cure extents of CB containing compounds are considerably higher with compared to previous others (compounds without CB). However, HNTs and IA loading adversely affects cure extent of the compounds with CB, systematically. If H0/C40/IA0.5 and H10/C30/IA0.5 compounds are considered and compared, it can be seen that MH value decreased by 10 phr replacing HNTs with CB. Decreasing of cure extent value of H10/C30/IA0.5 supports this finding. Also the CRI value of H10/C30/IA0.5 is higher than H0/C40/IA0.5. So H10/C30/IA0.5 compound needs more time to cure. Increase in IA amount causes some decrease in MH and cure extent values as can be seen from the relating property values of H10/C30/IA0.5 and H10/C30/IA1. Also,

H10/C30/IA1 has higher CRI value. It can be said that, IA is effective on mechanical properties, cure extent and CRI for containing CB compounds.

Table 4.4 : Rheological properties of compounds (with CB for 100 phr SBR).

	H0/C40/IA0	H0/C40/IA0.5	H0/C40/IA1	H10/C30/IA0.5	H10/C30/IA1	H20/C20/IA1
ML (dNm)	1.2	1.2	1.2	1.2	1.2	1.1
MH (dNm)	9	8.1	7.4	7.1	6.5	5.4
t_{s2} (min)	1.0	1.0	1.0	1.1	1.1	1.2
t_{90}(min)	2.3	2.2	2.3	2.2	2.2	2.1
Cure extent	7.9	6.9	6.2	5.9	5.3	4.3
CRI (min^{-1})	76.9	81.2	72.5	86	89.6	111.5

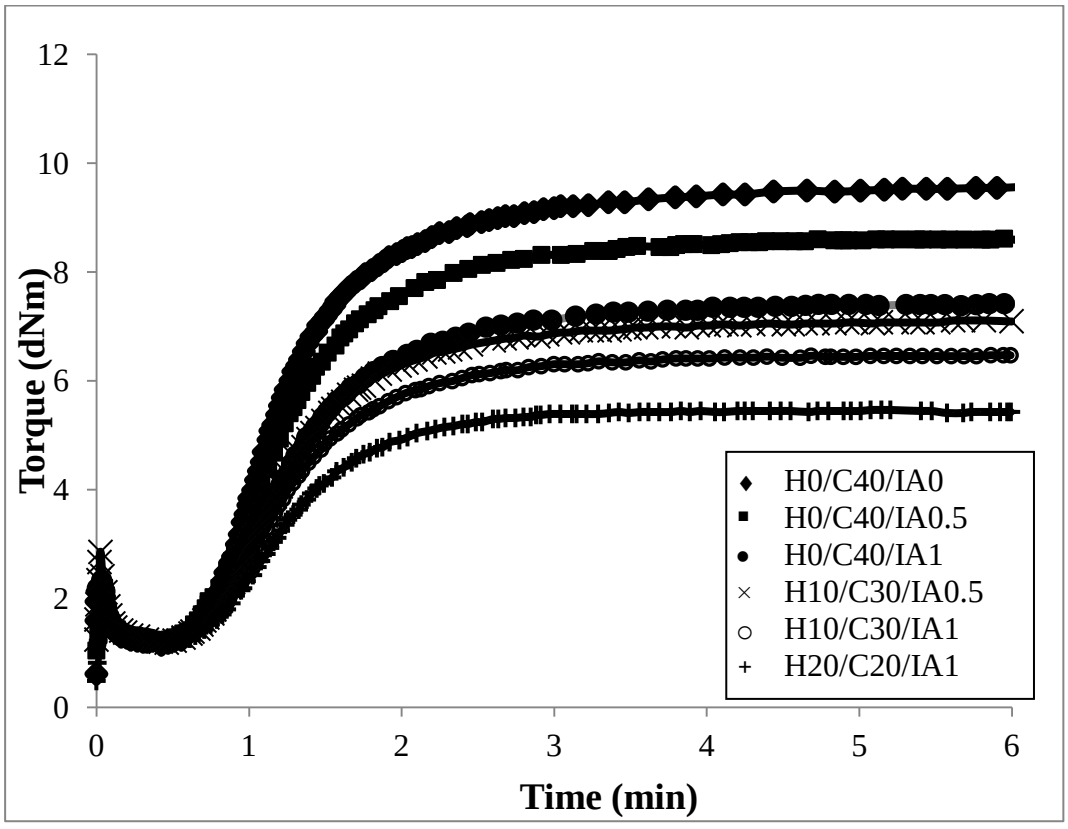


Figure 4.6 : Rheometer curves of the compounds without CB for 100 phr SBR at 180 ^{o}C.

Before mechanical tests and morphological measurements, T_g values and curing peak temparatures of compounds determined with a DSC. It is concluded that, T_g values of compound did not change significantly by adding HNTs, IA or CB. On the other hand, curing peak temperatures of compounds are affected by IA and CB amounts. While the curing peak temperature was increased by IA adding, CB caused a decrement for it. MDR results affirmed these determinations. CB provided moderate optimum cure times and enhanced MH values but HNTs or IA incorporation causes a systematic decrease in optimum cure times. Optimum cure times of H0/IA5, H20/IA5 and H30/IA5 are 10 times higher than the other compound. This finding supports their high curing peak temperatures which determined by DSC.

Table 4.5: Young's modulus, tensile strength and elongation at break values of nanocomposites without CB for 100 phr SBR

	Young's Modulus (E, Mpa)	**Tensile Strength (σ, Mpa)**	**Elongation at break (ε, %)**
H0/IA0	1.3	1.6	377.2
H20/IA0	1.1	1.9	487.8
H20/IA0.5	1.0	1.4	574.5
H20/IA1	1.0	1.5	651.8
H20/IA2	0.9	1.4	909.2
H30/IA0	1.0	1.8	566.6

Curing and molding were performed on a hydraulic press for their own optimum cure times which obtained with MDR at 180 ^{o}C. Nanocomposites were taken from the moulds and test samples were prepared in required dimensions from the sheets with using sharp knives.

4.3 Mechanical Properties of Nanocomposites

4.3.1 Tensile tests

Tensile tests were done by using tensile test equipment according to ASTM D 412 and he error margins calculated as as mentioned in Section 3.3.4.1. Without CB – with CB nanocomposites were evaluated separately.

Young's modulus, tensile strength and elongation at break values of nanocomposites without CB can be seen from Table 4.5.

For compounds without CB, HNTs incorporation provides slightly enhanced tensile strength values but this increment is not remarkable. A small decrement in tensile strength of H30/IA0 (with compared to H20/IA0) may be attributed to hard diffuse of HNTs in SBR matrix. On the other hand, Young's modulus values were not changed significantly by HNTs adding. Increasing HNTs loadings give gradually high elongation at break values. This may be explained with lower stiffness effect of HNTs. IA adding caused rising on elongation at break values up to 140%. H20/IA2 demonstrated maximum elongation at break value, 909.2%. Figure 4.7 shows comparison of tensile strength and elongation at break values of nanocomposites without CB. It can be seen that, elongation at break values increase by adding IA.

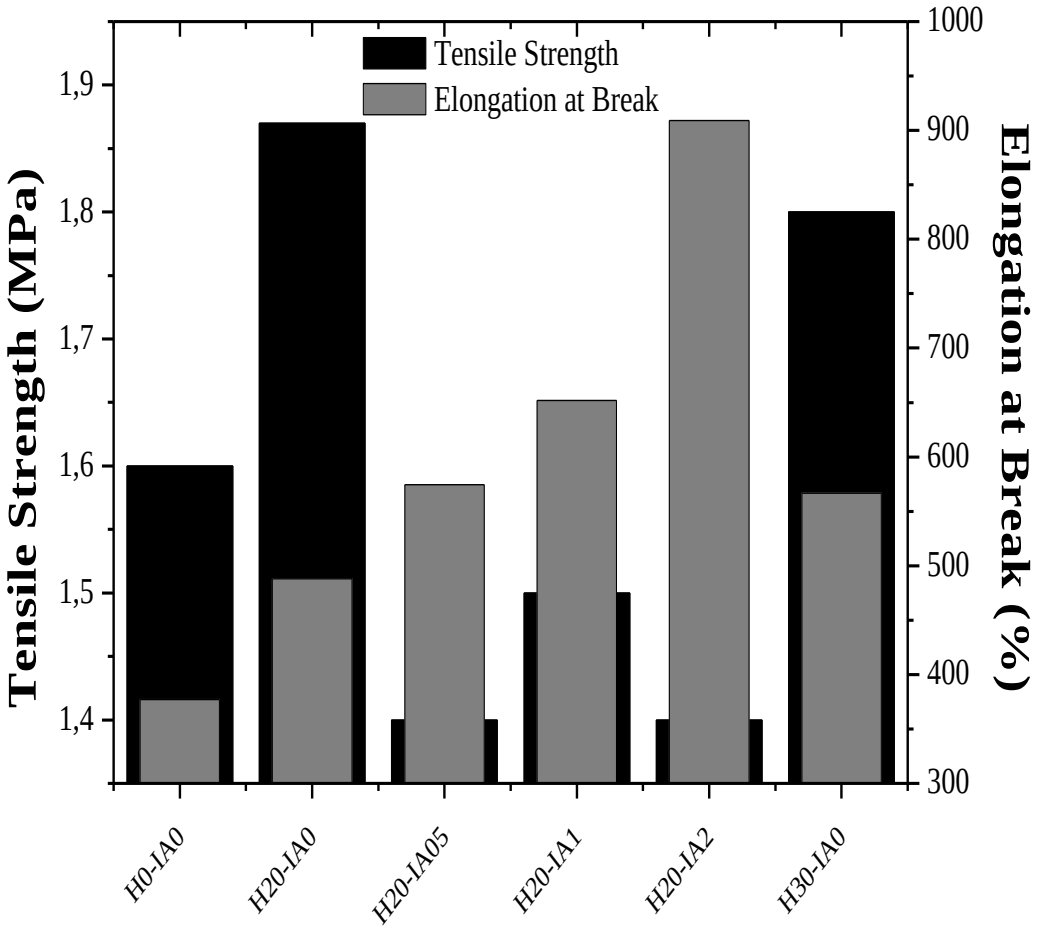


Figure 4.7 : The effect of HNTs and IA amounts on tensile strength and elongation at break values of the nanocomposites without CB for 100 phr SBR.

Table 4.6 : Young's modulus, tensile strength and elongation at break values of nanocomposites with CB for 100 phr SBR.

	Young's Modulus (E, Mpa)	Tensile Strength (σ, Mpa)	Elongation at break (ε, %)
H0/C40/IA0	1.9	8.3	570.1
H0/C40/IA0.5	1.8	7.9	560.6
H0/C40/IA1	1.4	6.7	569.1
H10/C30/IA0.5	0.8	5.2	619.0
H10/C30/IA1	0.9	5.4	598.1
H20/C20/IA1	0.4	3.7	712.0

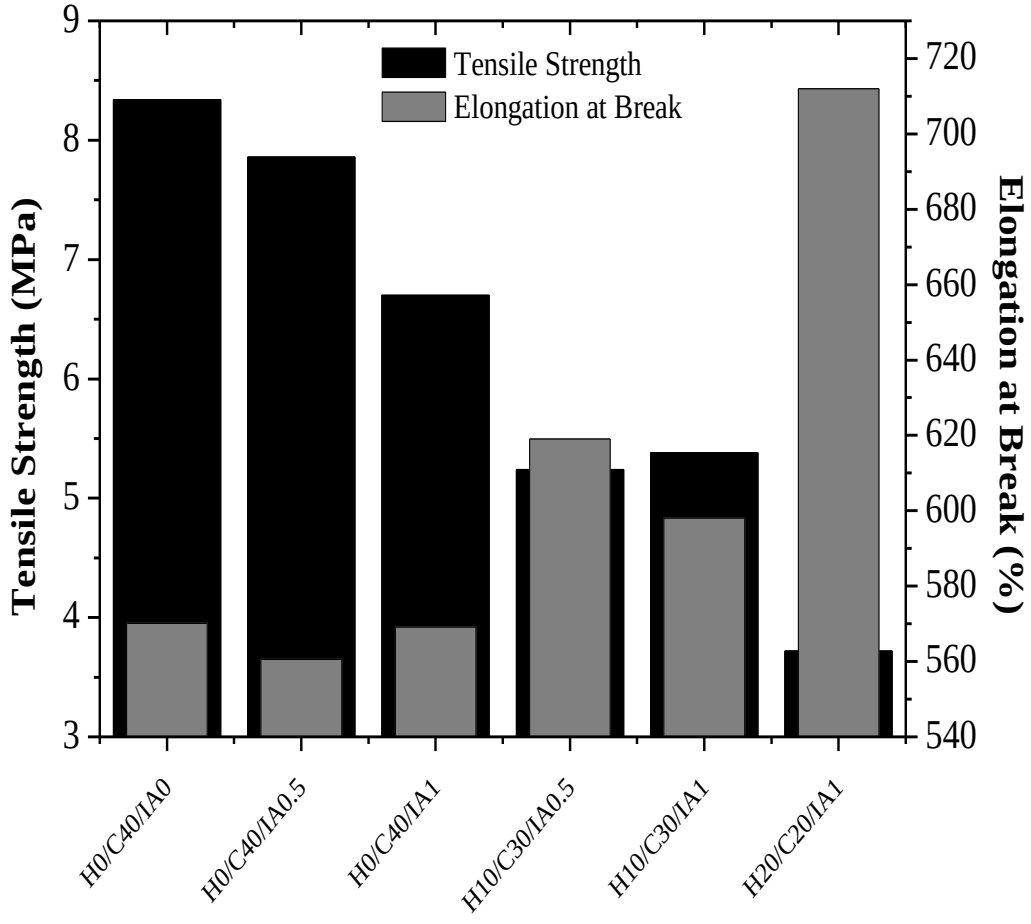


Figure 4.8 : The effect of HNTs and IA amounts on tensile strength and elongations at break values of the nanocomposites with CB for 100 phr SBR.

CB addition to SBR/HNTs compounds was done to evaluate effect of CB on compounds which include HNTs or IA. As can be seen Table 4.6 and Figure 4.8,

using HNTs instead of CB caused nearly 20% decrement in tensile strength. For H0/C40/IA0, H0/C40/IA0.5 and H0/C40/IA1 compounds, it can be clearly seen from Table 4.6 that, IA was reduced the tensile strength and values but elongation at break and Young's modulus values did not change for this compounds, significantly. For H10/C30/IA0.5 and H10/C30/IA1 compounds, there was not a remarkable difference between Young's modulus, tensile strength and elongation at break values. H20/C20/IA1 has minimum Young's modulus and tensile strength values but elongation at break value was maximum for this compound. When IA amount is taken constant, it is clearly seen that increasing amount of HNTs (H0/C40/IA05-H10/C30/IA05 and H0/C40/IA1-H10/C30/IA1-H20/C20/IA1) deteriorates tensile strength of the nanocomposites as in the range of 20-33%. Beside this, increase in elongation at break values for the same nanocomposite groups is 5-20%. This behavior also proves lower stiffness effect of simply HNTs with compared to CB which gives better interaction with the rubber matrix. Young modulus values of with CB nanocomposites decreased by HNTs and IA adding.

If without CB and with CB compounds are compared, H20/IA1 and H20/C20/IA1 compounds can be evaluated. The tensile strength of H20/C20/IA1 is higher than that of H20/IA1 owing to CB. Beside this, elongation at break value of H20/C20/IA1 is higher, too. Young's modulus value of H20/C20/IA1 is lower than H20/IA1.

4.3.2 Crosslinking densities of nanocomposites

Crosslinking densities of nanocomposites (CLDs) are determined with Young's modulus (E) approach which the numerical results are obtained from tensile tests as mentioned at Section 3.3.4.2. The CLD values can be seen Table 4.7. It is found to get lower CLD values for HNTs containing compounds with increasing amount of HNTs and also IA incorporation slightly reduces the crosslinking capacity of the compounds. There is 12% percent decrement when compared H0/IA0 and H20/IA0 compounds are compared. For the compounds with CB, there is an enhancement for CLD values. It is pointed out 47% increment between H0/IA0 and H0/C40/IA0. There is a relatively sharper decrement by adding HNTs in CLD values. Hence, as explained before, those nanocomposites with higher HNT contents show insufficient interaction with rubber. Due to weak interactions between HNTs and rubber caused less crosslinking density for nanocomposites with more HNTs contents. However, effect of IA incorporation on

CLDs is not as appreciable (as that of HNTs incorporation) for same HNTs levels in dual filler systems. Results are also in good consistence with cure extent values which are obtained with MDR of the corresponding compounds. This can be attributed to HNTs and IA hinders the interaction between rubber chains in physical manner and also weak interaction between HNTs and rubber as compared with that of CB.

Table 4.7 : Crosslinking densities of nanocomposites for 100 phr SBR.

	Crosslinking Densities (mol/m^3)
H0/IA0	169.5
H20/IA0	149.3
H20/IA0.5	141.3
H20/IA1	138.6
H20/IA2	121.1
H30/IA0	145.3
H0/C40/IA0	250.2
H0/C40/IA0.5	238.1
H0/C40/IA1	192.4
H10/C30/IA0.5	113.0
H10/C30/IA1	122.4
H20/C20/IA1	55.2

4.3.3 Hardness tests of nanocomposites

Hardness values of nanocomposites were measured with a Shore A type durometer and results were evaluated as follows.

Existence of HNTs exhibits a slight hardness decrement in various percentages of both with and without CB compounds as it can be seen from Table 4.8. This is because nanocomposites with more HNTs show lower stiffness than nanocomposites with more CB. This finding overlaps with mechanical test results. Stiffness and hardness of nanocomposites reduced its resilience and toughness, which further leads to lower elongation at break. CB containing compounds have higher hardness values with compared to others, as expected. Rubber-filler interaction shows decreasing

trend as carbon black loading in composite is decreased. Better good interaction between CB and SBR matrix has been realized when compared to HNTs. This indication matches with CLD values of nanocomposites. CB exhibits a high dispersive component due to its surface area and that is low polarity a component. But, HNTs had low dispersive component and high polar component. It means that carbon black gives strong rubber-filler interaction and weak filler-filler interaction.. Again, this result shows that carbon black is more reinforcing filler than HNTs [47]. Hardness is also not affected considerably by IA incorporation.

Table 4.8 : Hardness values of nanocomposites for 100 phr SBR.

	Hardness (Shore A)
H0/IA0	35.8
H20/IA0	30.8
H20/IA0.5	29.6
H20/IA1	30.5
H20/IA2	26.0
H30/IA0	32.5
H0/C40/IA0	47.5
H0/C40/IA0.5	43.8
H0/C40/IA01	42.4
H10/C30/IA0.5	39.6
H10/C30/IA1	41.7
H20/C20/IA1	33.3

4.4 Morphological Properties of Nanocomposites

Morphological properties of nanocomposites were obtained by the method given in Section 3.3.4.4 from the tensile fractured surfaces for selected samples. These SEM micrographs are shown in Figures 4.9, 4.10 and 4.11. In Figure 4.9, it is clearly seen that, when H20/IA0 and H20/IA0.5 compounds are compared to each other, better dispersion behavior for HNTs can be achieved in SBR matrix owing to presence of IA. On the other hand, high HNTs amounts (e.g. 30 phr) cause considerable agglomerations (Figure 4.9, (c)). As it is depicted in Figure 4.10, IA has not considerable effect on CB dispersion in SBR matrix. However, for the same IA amount (1 phr) in CB containing

compounds, as seen in Figure 4.11, it can be said that increasing HNTs content has negative contribution to dispersion of the filler system in the compound matrix. This result also coincides with MDR measurements, tensile test results and CLD measurements. IA has good dispersing effect for HNTs but this affirmative indication did not overlap the DSC, MDR, tensile and hardness test results.

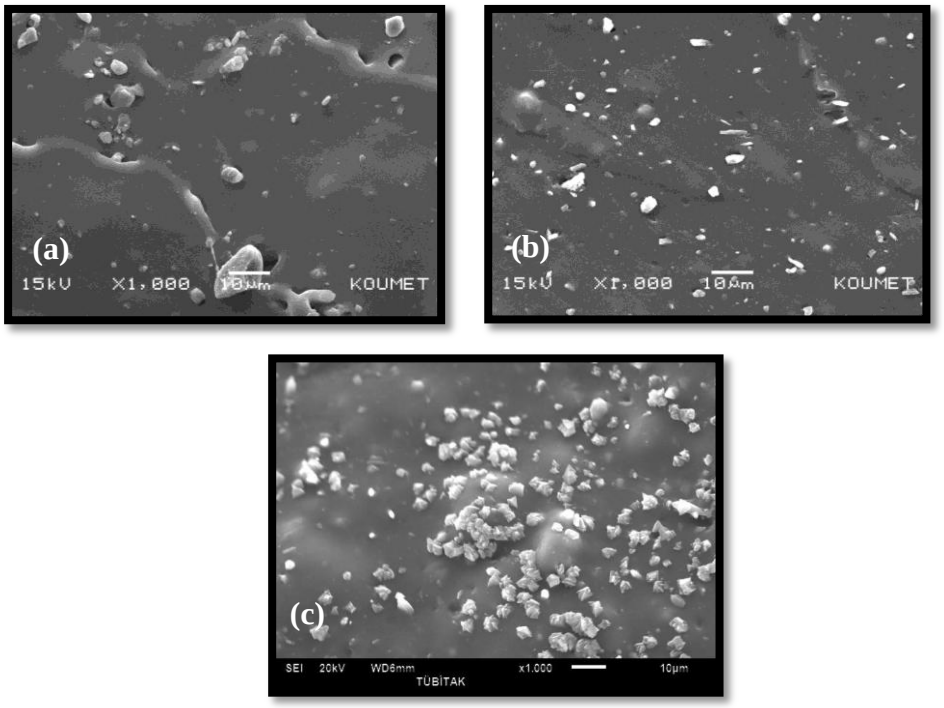


Figure 4.9 : SEM images of nanocomposites for 100 phr SBR **(a)** H20/IA0, **(b)** H20/IA0.5, **(c)** H30/IA0.

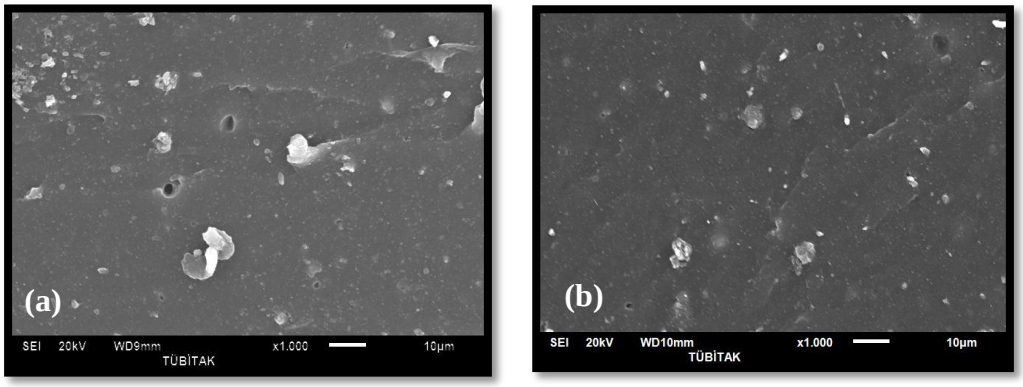


Figure 4.10 : SEM images of nanocomposites for 100 phr SBR **(a)** H0/C40/IA0, **(b)** H0/C40/IA0.5.

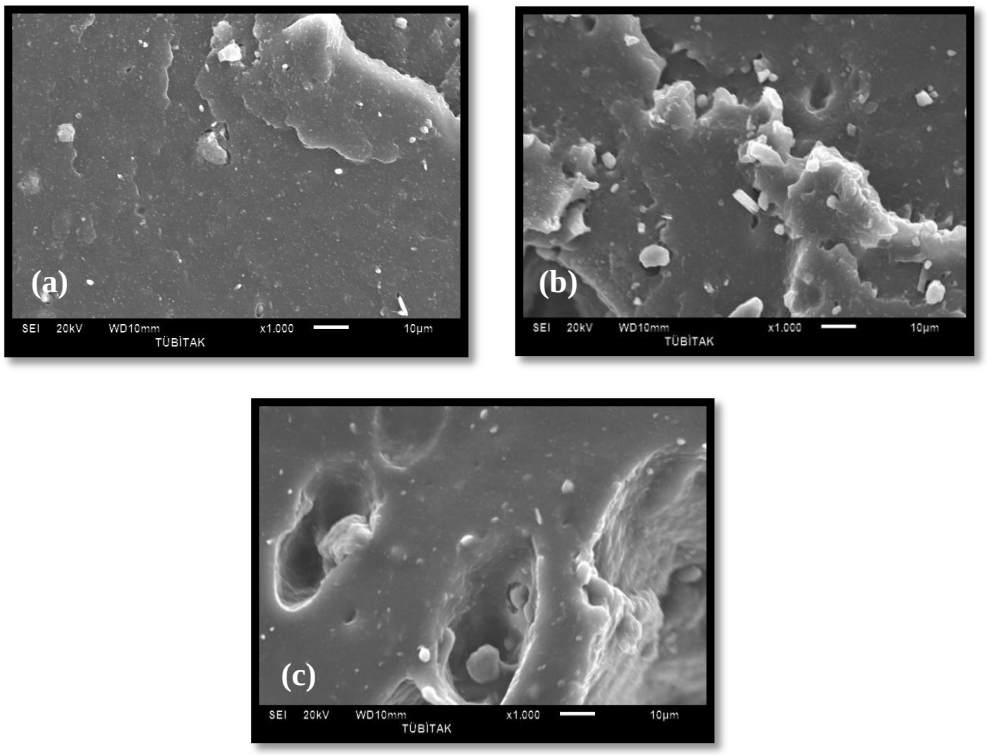


Figure 4.11 : SEM images of nanocomposites for 100 phr SBR **(a)** H0/C40/IA1, **(b)** H10/C30/IA1, **(c)** H20/C20/IA1.

4.5 Limiting Oxygen Index (LOI) Measurements Results of Nanocomposites

The flammability properties of H20/IA0 and H20/IA1 determined with LOI measurements. The LOI values of SBR compound (H0/IA0) were found in literature as 22±0.5 [52].

It was described 28.00 < LOI < 100 as being ``self-extinguishing'' while the threshold LOI=20.95 define the material as``marginally stable''. Fenimore, refers to materials that are between the marginally stable and self-extinguishing thresholds, i.e. 20.95< LOI< 28, as being ``slow-burning'' [53].

LOI values of H20/IA0 and H20/IA1 nanocomposites were determined as 28±0.5. According to the these results, H20/IA0 and H20/IA1 nanocomposites for 100 phr SBR can be regarded as self-extinguishing material..

5. CONCLUSION

In this study, IA was used as a modifier for SBR/HNTs compounds prepared with and without using CB. 15 compounds were prepared at laboratory type two roll mill and they had different ingredients (HNTs amount was between 0-30 phr and IA amount was between 0-5 phr for compounds which are without CB. HNTs amount was 0-20 phr, IA amount was 0-1 phr and CB amount was 20-40 phr for compounds which are with CB). Their thermal properties were examined at DSC, optimum curing times and cure characteristics were determined with a MDR. H0/IA5, H20/IA5 and H30/IA5 compounds were not cured because of their unsatisfactory DSC and MDR results. They give higher curing peak temperatures and curing times when compared with other compounds. The mechanical, morphological and hardness measurements could not be practiced for them. Mechanical properties obtained from a tensile tester, hardness values determined with a Shore A type durometer and morphological properties were obtained from SEM measurements. The obtained results are summarized below.

T_g values was almost same for all compounds as explained at Section 4.1. In other respect, the existence of IA is effective on optimum curing temperatures of SBR based rubber compounds and it causes a significant delay in curing reaction for compounds without CB. IA affects the curing peak temperature for compounds with CB; however, this effect is not as significant as SBR/HNTs nanocomposites. Another result for thermal properties; IA should be optimized to have satisfactory curing characteristics. MDR measurements indicated that ML values of all compounds can be assumed as unchanged. On the other hand, MH values decrease significantly by loading HNTs and also IA. HNTs cause a decrement for optimum cure times. However, IA affects optimum cure time by a slight increase, especially after 1 phr loading. Optimum cure times of H0/IA5, H20/IA5 and H30/IA5 are 10 times higher than the other compounds. This finding supports their high curing peak temperatures which determined DSC. So, these compounds were not cured for other measurements. For compounds with CB, cure extents of CB containing compounds are considerably higher with compared to previous

others (compounds without CB). It can be said that, CB exhibits better reinforcing filler behavior than HNTs. However, HNTs and IA loadings adversely affect cure extent of the compounds with CB, systematically. It is concluded from tensile test results that, HNTs incorporation provides slightly enhanced tensile strength values for compounds without CB. Increasing HNTs loadings give gradually higher elongation at break values. Another result for tensile test, increase in elongation at break values for the same nanocomposite groups is 5-20%. This behavior also proves lower stiffness effect of simply HNTs with compared to CB which gives better interaction with the rubber matrix for tensile test results. It means that CB gives strong rubber-filler interaction and reinforcement. Crosslinking densities (CLD) of nanocomposites are obtained from young modulus values. It is found to get lower CLD values for HNTs containing compounds with increasing amount of HNTs and also IA incorporation slightly reduces the crosslinking capacity of the compounds. For the compounds with CB, there is a relatively sharper decrement by adding HNTs in CLD values. Those nanocomposites with higher HNTs contents show weak interaction with rubber. Due to weak interactions between HNTs and rubber caused less crosslinking density for nanocomposites with more HNTs contents. These results overlapped poor curing characteristics and mechanical properties of compounds which include IA. CB containing compounds have higher hardness values with compared to others, as expected. Rubber-filler interaction shows decreasing trend as CB loading in composite is decreased. It shows good interaction between CB and SBR matrixes when compared to HNTs. This indication matches with tensile test results, hardness and CLD values of nanocomposites. Hardness is also not affected considerably by IA incorporation. It is clearly seen from SEM micrographs that, better dispersion behavior for HNTs can be achieved in SBR matrix owing to presence of IA. On the other hand, high HNTs amounts (e.g. 30 phr) cause significant agglomerations. IA has not considerable effect on CB dispersion in SBR matrix. However, for the same IA amount in CB containing compounds, it can be said that increasing HNTs content has negative contribution to dispersion of the filler system in the compound matrix. This result also coincides with MDR measurements, tensile test results and CLD measurements. IA has good dispersing effect for HNTs but this affirmative indication did not overlap the DSC, MDR, tensile and hardness test results. According to LOI results, adding of HNTs to SBR for preparing of nanocomposites made the flammability properties from slow-burning to self-extinguishing materials.

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